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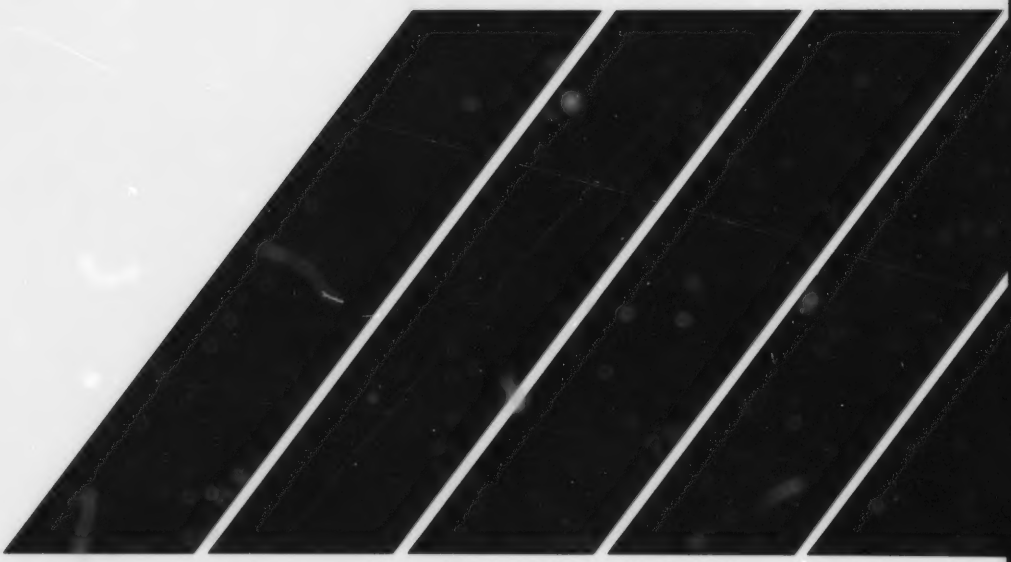

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PRODUCTION OF HYDROCARBONS FROM BIOMASS USING THE WATERLOO FAST PYROLYSIS PROCESS

PREPARED FOR:

Efficiency and Alternative Energy Technology Branch
Energy, Mines and Resources Canada
Ottawa, Ont.
DSS File No. 23283-8-6067
January, 1991

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98 pp

92-06670/

CITATION

Scott, D.S., Dept. of Chemical Engineering, University of Waterloo. *Production of Hydrocarbons from Biomass Using the Waterloo Fast Pyrolysis Process*. DSS Contract No. 23283-8-6067. Efficiency and Alternative Energy Technology Branch, Energy, Mines and Resources Canada, Ottawa, Ontario. 1991 (98 pp.)

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NOTE

Funding for this project was provided by the Federal Panel on Energy Research and Development, Energy, Mines and Resources Canada.

© Minister of Supply & Services Canada 1992
Catalogue No. M91-7/177-1992E
ISBN 0-662-19739-9

ACKNOWLEDGEMENTS

The authors would like to express their thanks to Sarah L. Mason whose studies of catalytic hydropyrolysis carried out as a part of her MASc program contributed to the results given in this report. Our thanks are also expressed to the Alternative Energy Branch of Energy, Mines and Resources for financial support of this work, and to Dr. David Fung of CANMET for his advice and assistance as scientific liaison officer. Appreciation is also expressed to the Natural Sciences and Engineering Research Council of Canada for support of fundamental studies, some of which are also included in this report.

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EXECUTIVE SUMMARY

Earlier work in this laboratory had shown that it was possible to hydrogasify wood directly at atmospheric pressure in a fluidized bed of nickel catalyst at operating conditions corresponding to those that were optimal for maximum liquid yields in the Waterloo Fast Pyrolysis Process (WFPP). Methane yields equivalent to 70 to 75% biomass carbon conversion were achieved. It was conceived that it might be possible to produce higher hydrocarbons by the same method with suitably modified catalysts. Hence, the major objective of the present work was to investigate the possibility of direct single step production of light hydrocarbons (C_2+) from wood or cellulose by a process which we call "Catalytic hydropyrolysis".

A wide range of catalytic metals, singly or in combination, - Fe, Ni, Co, Zn, Zr, Cr, Mo, W, Si, Al, Ti and Mg - have been investigated for this type of catalytic activity, as well as three supports. The catalyst screening tests reported here cover not only results developed as a part of the contract studies, but also many results obtained in our laboratory by graduate students or other researchers pursuing more fundamental studies.

The best performances for hydropyrolysis of wood and cellulose were obtained from Co/Mo catalysts on alumina supports

which gave yields of up to 24% by weight of the poplar wood fed of C_2+ hydrocarbons, and up to 15% of C_4+ hydrocarbons, representing about a 40% biomass carbon conversion. Relatively small amounts of methane were produced (4% to 6%), and if these are included, the maximum carbon conversion to light hydrocarbons approached 50%. In addition, small yields of liquid were obtained (4% to 12%) which were heavier hydrocarbons, phenolics or ketones of low oxygen content.

Some conclusions about mechanisms can be drawn. In summary, it is clear that the reaction is a thermal pyrolysis followed by catalytic conversion **in situ** by the fluidized catalyst. Hence, the highest hydrocarbon yields tend to be obtained at the same conditions as those giving high volatile yields for thermal pyrolysis.

The product spectrum can be changed very significantly by the use of other supports. With alumina, the C_2 to C_7 fraction is highly olefinic, but other supports can increase the yield of aromatics or paraffins. Use of a hydrogen-donor, free radical atmosphere (propane) did not succeed in improving yields. The use of synthesis gas (1:1 $CO:H_2$) in place of hydrogen was also unsuccessful because the active catalysts also promoted the conversion of CO to CO_2 + C, and the resultant secondary carbon deposited on the catalyst. Pressure operation to three atmospheres absolute was tested also and yields of CH_4, CO and CO_2

decreased while heavy hydrocarbons, phenolics, etc. increased considerably. Yields of light hydrocarbons (C_2+) were not significantly affected. The use of a larger-pored zeolite catalyst with nickel did not succeed in increasing the yield of light C_4+ hydrocarbons, particularly BTX, as hoped, but gave significant yields of heavier products.

This work represents a new type of biomass pyrolysis process (catalytic hydropyrolysis) not previously investigated, which can give significant yields of light olefinic hydrocarbons in the C_2 to C_7 range directly from lignocellulosics. The economic significance of the work cannot yet be easily evaluated because long-term catalyst life testing and larger scale operation are still required. However, we believe this work opens up a previously unexplored area of research in the conversion of biomass to higher value energy production.

A second objective of this contract was to explore the behaviour of starches and grains in the WFPP. Cornstarch pyrolysis was difficult because of the low melting point of the material. However, total liquid yields of 80% to 90% were obtained, with 70% to 80% of the starch fed recovered as organic liquid. Corn kernels gave somewhat lower organic liquid yields (65%). Gas yields were low for both feeds (3% to 9%).

Catalytic hydropyrolysis of cornstarch, corn kernels and semolina was also attempted. Poor performance due to the hot feeding tube and agglomeration in the fluid bed made it impossible to obtain quantitative data except for granular cornstarch. Over Co/Mo catalyst yields from this feed were similar to those from wood or cellulose, except for a little lower yield of the C_4+ hydrocarbon fraction.

RÉSUMÉ

Les travaux antérieurs effectués dans notre laboratoire ont montré qu'il était possible d'hydrogazéifier le bois directement à la pression atmosphérique par catalyse sur nickel en lit fluidisé, à des conditions de fonctionnement correspondant aux conditions optimales donnant le rendement maximum en liquide dans le procédé à pyrolyse rapide de Waterloo (PPRW). Des rendements en méthane équivalant à la transformation de 70 à 75 % de la biomasse de carbone ont été atteints. On a fait l'hypothèse qu'il était possible de produire des hydrocarbures plus lourds par la même méthode en modifiant adéquatement le catalyseur. Par conséquent, les présentes recherches avaient pour principal objectif d'étudier la possibilité de produire directement en une seule étape des hydrocarbures légers (C_2+) à partir de bois ou de cellulose selon un procédé que nous avons nommé "hydropyrolyse catalytique".

On a étudié l'action catalytique d'une vaste gamme de catalyseurs métalliques - Fe, Ni, Co, Zn, Zr, Cr, Mo, W, Si, Al, Ti et Mg -, seuls ou en mélage, ainsi que trois supports. Les essais qui sont mentionnés ici ont été réalisés pour la sélection du catalyseur non seulement dans le cadre des études effectuées à contrat, mais aussi de recherches faites par des étudiants de deuxième ou de troisième cycle travaillant dans nos laboratoires ou par d'autres chercheurs à un niveau plus fondamental.

Les meilleurs rendements d'hydropyrolyse du bois et de la

cellulose ont été obtenus avec des catalyseurs de Co/Mo sur supports d'alumine : jusqu'à 24 % (en masse) de la charge de bois de peuplier en hydrocarbures C_2 et jusqu'à 15 % en hydrocarbures C_4+, ce qui représente une transformation d'environ 40 % de carbone de la biomasse. Des quantités relativement faibles de méthane furent produites (de 4 à 6 %); en les incluant dans le calcul du rendement, la transformation maximale du carbone en hydrocarbures légers atteignait presque 50 %. En outre, des petites quantités de liquide ont été obtenues (de 4 à 12 %); elles étaient constituées d'hydrocarbures plus lourds, de phénols ou de cétones à faible teneur en oxygène.

Nous pouvons tirer certaines conclusions concernant le mécanisme. En résumé, il est évident que la réaction est une pyrolyse thermique suivie d'une transformation catalytique *in situ* par le catalyseur fluidisé. Voilà pourquoi les meilleurs rendements en hydrocarbures ont tendance à survenir dans les conditions qui donnent un rendement élevé en composés volatils lors de la pyrolyse thermique.

L'emploi d'un autre support permet de faire varier de façon très significative la composition du produit. Sur alumine, la fraction allant de C_2 à C_7 est riche en oléfines, mais l'utilisation d'une autre support peut faire augmenter le rendement en composés aromatiques ou paraffiniques. Le travail sous une atmosphère de propane (production de radicaux libres, donneurs d'hydrogène) n'a

pas permis d'améliorer le rendement. L'utilisation d'un gaz synthétique (mélange CO:H_2 1:1) à la place de l'hydrogène s'est avérée, elle aussi, infructueuse parce que les catalyseurs activés entraînaient aussi la transformation du CO en CO_2 + C, avec dépôt du carbone secondaire produit sur le catalyseur. On a aussi fait des essais sous des pressions absolues atteignant trois atmosphères : le rendement en CH_4, en CO et en CO_2 diminuait et celui en hydrocarbures lourds, en phénols, etc. augmentait considérablement. Le rendement en hydrocarbures légers (C_2+) n'était pas modifié de façon significative. Contrairement à nos attentes, l'utilisation avec le nickel d'un catalyseur de zéolite à pores plus larges n'a pas permis d'augmenter le rendement en hydrocarbures C_4+ légers, en particulier en BTX; toutefois, des rendements significatifs en produits lourds furent obtenus.

Ces recherches représentent un nouveau type de procédé de pyrolyse de la biomasse (hydropyrolyse catalytique) qui n'avait jamais encore été étudié et qui peut donner directement des rendements significatifs en hydrocarbures oléfiniques légers allant de C_2 à C_7 à partir de substances lignicellulosiques. Il n'est pas encore possible d'évaluer facilement la valeur monétaire de ces recherches, car il faudra encore procéder à des essais à long terme de la durée du catalyseur ainsi qu'à des essais en vraie grandeur. Toutefois, nous croyons que ces travaux ouvrent un domaine de recherche jusqu'ici inexploré en matière de transformation de la biomasse en produits ayant une plus grande valeur énergétique.

Le présent contrat avait aussi un second objectif : étudier la réactivité des fécules et des céréales dans le PPRW. La pyrolyse de la fécule s'est avérée difficile vu son bas point de fusion. Toutefois, des rendements variant de 80 à 90 % en liquide total ont été obtenues, de 70 à 80 % de la charge de fécule étant récupérée sous forme de liquide organique. Avec des grains de maïs, le rendement en liquid organique était quelque peu moindre (65 %). Les rendements en gaz obtenues avec ces deux charges étaient bas (de 3 à 9 %).

On a aussi tenté de faire l'hydropyrolyse de fécule, de grains et de semoule de maïs. La chaleur du tube d'alimentation et l'agglomération de la charge dans le lit fluidisé ont entraîné un mauvais fonctionnement, de sorte qu'il fut impossible d'obtenir des données quantitatives sauf dans le cas de la fécule de maïs en grain. Avec cette charge, les rendements sur catalyseur de Co/Mo étaient semblables à ceux obtenues avec le bois ou la cellulose, si ce n'est une légère augmentation de la fraction en hydrocarbures C_4+.

PRODUCTION OF HYDROCARBONS FROM BIOMASS USING THE WATERLOO FAST PYROLYSIS PROCESS

Final Contract Report No. 23283-8-6067/01-SZ

by Donald S. Scott, Jan Piskorz, Desmond St.A.G. Radlein
Stefan R. Czernik and Piotr Majerski

1. INTRODUCTION

In an earlier contract report (Catalytic Hydrogasification of Wood, Contract No. 24ST-23216-4-6365, March, 1986) we showed that it was possible to hydrogasify wood in a fluidized bed reactor at atmospheric pressure with hydrogen at the optimal Waterloo Fast Pyrolysis conditions. Using nickel on alumina catalysts, 70% to 75% of the carbon in the wood could be converted to methane at 500° to 550°C, to yield a gas with over 90% methane by volume. This discovery was used as the basis for a proposed new biomass gasification system. However, no further development was funded or carried out with respect to this technology.

In subsequent work by a graduate student (S. Mason) in our laboratories, it was found that using Co/Mo catalysts minimized methane production and enhanced the production of C_2+ compounds, with 20% to 25% of the biomass carbon appearing as C_4+ material. These preliminary results were the justification for the more extensive evaluations of this direct conversion of biomass to hydrocarbons by WFPP technology, which is the major effort reported here.

A secondary study was carried out on the pyrolysis and hydrogasification of starch and grain, inasmuch as the natural carbohydrate polymers based on amylose had never been investigated in the WFPP before.

2. OBJECTIVES

The original objectives of this work as outlined in May, 1989, had to be modified considerably as the research progressed, both because of discouraging results in some cases, and in other instances to re-direct the work into more promising avenues. In particular, one original objective which required the pilot plant to be modified for hydrogasification was abandoned because the cost and danger were not commensurate with any knowledge which might be gained. Another original tentative objective was to attempt hydrogasification of an aqueous effluent, but this was not pursued after early evaluation of a real case showed that it would be uneconomical.

The original objectives included not only studies of hydrogasification or hydrodeoxygenation, but also pyrolysis studies of starch or starchy material.

Objectives of this work can be summarized as follows;

1. To further investigate the hydrogasification of biomass (wood or cellulose) to determine the conditions and catalyst which might maximize yields of C_2+ hydrocarbons at WFPP conditions. Process variables to be investigated were;

a. The effect of pressure on conversion,

b. The use of CO/H_2 synthesis gas in place of hydrogen,

c. Investigation and comparison of Ni/Mo and Co/Mo catalysts,

d. From speculations on the reaction mechanism, to design alternative catalysts and to test them, using both different metals and different supports,

e. To investigate the use of an H-donor (a saturated hydrocarbon) rather than hydrogen.

2. To evaluate the behaviour of corn starch or whole corn kernels in thermal pyrolysis and in hydrogasification.

In addition to the above a new objective, which was not previously conceived, was accomplished.

3. Development of an active catalyst for low temperature gasification of biomass to synthesis gas.

3. METHODS AND PROCEDURES

The apparatus employed in the current studies has been described in earlier reports, e.g., Catalytic Hydrogasification of Wood, Contract 24ST-23216-4-6365, and details can be found there. All work described here was done using the bench scale (30 to 100 gm/h) fluidized bed unit. Descriptions and procedures used as well as analytical methods can also be found in several journal articles by Scott et al.

Because a variety of methods were employed in various aspects of this work, any unique apparatus and procedures used will be described in the "Results" section dealing with the particular subject. Methods of catalyst preparation, or specifications for commercial catalysts used are also given in the appropriate section.

4. CATALYTIC HYDROPYROLYSIS OF WOOD AND CELLULOSE

4.0 Introduction

A major objective of this contract was a preliminary exploration of the possibility of obtaining high yields of hydrocarbon fuels and chemicals from wood in a one-step atmospheric pressure catalytic flash pyrolysis process in a hydrogen atmosphere (hydropyrolysis). This concept is a direct outgrowth of the success of the WFPP in obtaining high liquid yields by fast pyrolysis of biomass (70% to 80%) in a bed of fluidized sand particles. Replacement of the sand by an appropriate nickel catalyst and by use of hydrogen atmosphere at WFPP optimal conditions was shown by Scott and by Garg et al. [1][2] to give carbon conversions to methane of up to 75%. Use of a cobalt catalyst in place of nickel suggested that less carbon could be converted to methane and more to C_2+ hydrocarbons. Initial work, therefore, explored this possibility. These initial tests also form the base-line results for the evaluation of the effects of process variables.

Some of the effects of catalyst composition, operating conditions and selected feedstocks on the yield of C_2+ components were studied in subsequent tests also using a bench scale pyrolysis unit.

A number of commercial catalysts were selected for use in this screening study, as well as three catalyst supports and additional catalysts prepared in our own laboratory and a sulphided commercial catalyst. The conditions selected for the screening experiments were 500°C, 0.50 to 0.60 seconds vapour residence time and F/C of about 1.00 g/ g h. Fe, Ni, Co, Zn, Zr, Cr, Mo, W, Si, Al, Ti and Mg were all considered as potentially catalytically active materials in either their oxide or reduced form, either singly or possibly in combination with other elements on one catalyst. Cellulose rather than wood was used for many of the screening experiments due to its importance as the major component of biomass feedstocks, as well as its well-defined composition which may allow easier interpretation of results.

4.1 Basic Tests with Ni and Co Catalysts

Experimental

Experiments with Avicel PH-102 cellulose and IEA Aspen Poplar were conducted to determine the effect on product composition of a change in feedstock and enhance understanding of possible modes of action of the catalyst.

A process flow diagram of the experimental system is shown in Figure 4.1. Hydrogen was used to transport the feedstock particles (cellulose or wood) continuously into the bench scale fluidized bed reactor at feed rates of 10 to 100 g/h. Hydrogen also entered the base of the reactor to fluidize the bed of catalyst particles (250 to 590 microns). The process operated under atmospheric pressure. All solid, liquid and gaseous products were collected, and a material balance was attempted. The concentrations of methane and carbon monoxide were continuously monitored as the experiment progressed.

The product recovery system was designed to permit a complete material balance to be obtained since each unit, as well as the connecting lines, could be disassembled and weighed before and after the experiment. The condensers and all the lines were washed with methanol at the conclusion of a run to obtain the "methanol solubles" composed of tar and water.

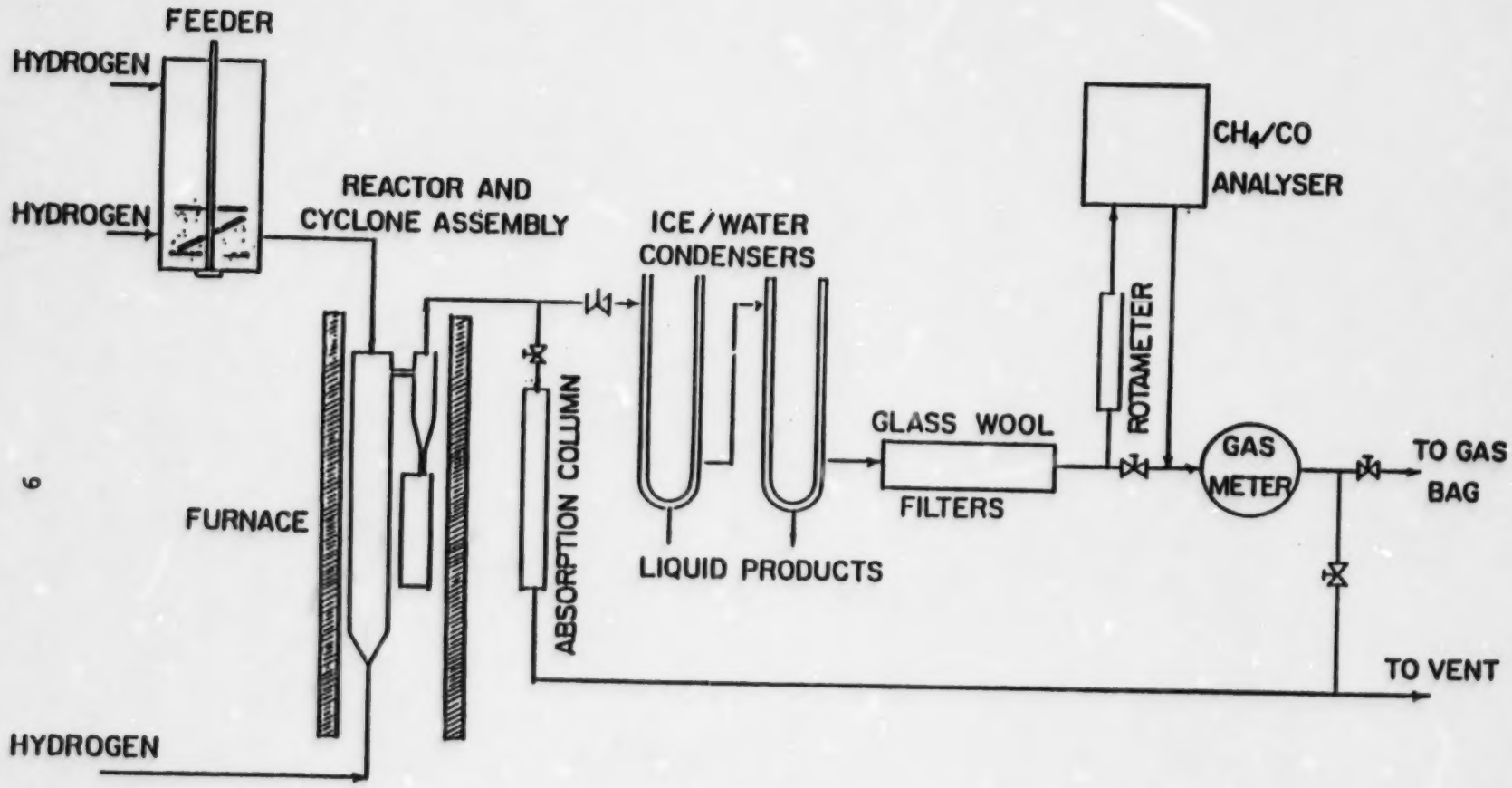


Figure 4.1 Process Flow Diagram for Catalytic Hydrogasification of Wood

Analysis of gases was carried out by gas chromatography, and identification of unknown materials was confirmed by GC/MS. Liquid product analysis was done by Karl Fischer titration for water and by GC/MS or HPLC for other components. Two different feed materials were studied: cellulose and poplar wood. Properties of these feedstocks are given in Tables 4.1 and 4.2.

The Avicel PH-102 microcrystalline cellulose used in this study is described by the manufacturer as a purified, depolymerized, alpha cellulose derived from fibrous plants, relatively free from organic and inorganic contaminants (less than 10 ppm heavy metals). The degree of polymerization reported by Piskorz et al. [3] (determined by the viscosity method using standard G-24P of the Canadian Pulp and Paper Association) was 227.

In the experiments with wood, International Energy Agency (IEA) Aspen Poplar standard sawdust was used. The sample was composed of 49.1% cellulose, 20.5% hemicellulose and 23.5% lignin, on a moisture and ash free basis [3].

Product yields are reported as % by weight of feed on a moisture and ash-free basis. Hydrogen atmosphere was used in nearly all the catalytic experiments. Usually, the experiments were of 30 minutes duration, employed 40 grams

Table 4.1

Data for PH-102 Avicel Cellulose Feedstock

Physical Properties and Elemental Analysis of PH-102 Avicel Cellulose

Element	% by weight <a>
Carbon	44.4
Hydrogen	6.2
Oxygen	49.3
Nitrogen	0.0
Ash	60.0 ppm
	100.0

Higher Heating Value, maf	4353 cal/g
Particle Size Range (microns)	74-149

<a> Dry basis - Formula C6H10O5

Table 4.2

Data for IEA Aspen Poplar Feedstock

Physical Properties and Elemental Analysis of IEA Aspen Poplar

Element	% by weight <a>
Carbon	48.5
Hydrogen	6.2
Oxygen	44.2
Nitrogen	0.7
Ash	0.4
	100.0

Higher heating value, maf	4661 cal/g
Particle Size (microns)	106-250

<a> Dry Basis

of catalyst in the fluidized bed and consumed 20 grams of feedstock (at a feed rate of about 40 grams per hour) fed continuously into the reactor.

Work previously reported from our laboratory [1] showed that direct methanation of wood was possible at one atmosphere pressure using a catalyst as the fluidized bed solid in a hydrogen atmosphere. A comparison of uncatalyzed pyrolysis and catalyzed pyrolysis with a Co-Mo catalyst is shown in Table 4.3. The interesting aspect of these results is the fact that over Co-Mo the production of methane is minimized, and there is a greatly increased yield of C_2+ hydrocarbons, representing about a 31% carbon conversion to C_2+ components, and a 38% carbon conversion to hydrocarbons including methane. In addition, some of the volatile liquid components boiling under about 80°C would be lost because of the method of recovery of the liquid fraction. It should be mentioned that the liquid (tar) recovered was heavier hydrocarbons, and not oxychemicals as in ordinary pyrolysis.

A comparison of results for a pure microcrystalline cellulose (Avicel) and for wood is shown in Table 4.4. Interestingly, the carbon conversions to C_2+ components is about the same for both, but because of its lower oxygen content, the weight percent yield of C_2+ hydrocarbons from wood is somewhat higher than that from cellulose.

Table 4.3

Effect of Catalyst and Atmosphere - Overall Yields

IEA aspen poplar (106-250μm), 497°C.

Run Number	22M	44M
Atmosphere	Nitrogen	Hydrogen
Catalyst: Name	Ottawa Sand	C20-6-04
Catalyst: Metal1	—	5.0% CoO
Catalyst: Metal2	—	19% MoO3
Catalyst: Support	—	Alumina
Residence Time (s)	0.63	0.59
F/C (g/gh)	0.53	0.50
Feed/Catalyst (g/g)	0.26	0.25
Feed Rate (g/h)	33.72	21.08
Total Yield of Components (% Weight of Feed maf Basis)		
CHAR:	14.70	9.93
TAR:	61.11	8.36
WATER:	12.17	33.26
TOTAL GAS:	13.99	42.95
Carbon Monoxide	5.03	13.43
Carbon Dioxide	6.96	7.09
Methane	0.34	4.39
Ethylene	0.15	2.51
Ethane	0.04	3.10
Propylene	0.07	2.73
Propane	----	0.81
Acetaldehyde	0.34	0.11
Butenes	0.05	0.84
Butanes	----	1.45
16.50 } unidentified	0.27	0.13
17.07 } unidentified	----	0.06
Cyclopentenes	----	3.08
Benzene	0.75	2.32
Toluene	----	0.91
Total Recovery (%):	101.96	94.51
Oxygen Balance (%):	42.42	95.91
Gas Carbon Selectivity (%):		
METHANE	4.43	12.68
C2+	24.31	57.66
HYDROCARBONS	28.74	70.34
Total Feed Carbon to Gas Component (Weight %):		
METHANE	0.52	6.79
C2+	2.85	30.87
HYDROCARBONS	3.37	37.65
% Coke on Catalyst:	0.3	1.0

TABLE 4.4

Comparison of Results for Cellulose and Wood

Alumina Support, 499° 0.57 s, hydrogen.

Run Number	27M	42M	50M	49M
Feed Type	Cellulose	Cellulose	Wood	Wood
C: Metal1	5.0% NiO	5.0% CoO	4.5%NiO	4.5%CoO
C: Metal2	19% MoO3	19% MoO3	14%MoO3	20%MoO3
F/C (g/gh)	1.18	1.12	0.64	0.62
Feed/Cat. (g/g)	0.59	0.56	0.33	0.33
Feed Rate (g/h)	45.42	46.08	26.32	26.19
NiO/MoO3	0.263	0.263	0.321	0.225
Total Yield of Components (% Weight of Feed maf Basis):				
CHAR:	4.85	4:12	10.74	14.41
TAR:	5.00	7.74	8.72	7.80
WATER:	40.71	38.59	31.71	32.04
TOTAL GAS:	47.41	41.99	46.86	46.32
CO	11.62	12.96	12.93	13.46
CO2	6.56	9.25	7.09	7.84
CH4	15.58	2:32	6.88	5.58
C2+	13.65	17.47	19.95	19.45
Total Recovery:	97.96	92.44	98.02	100.58
Oxygen Balance:	96.48	98.16	92.13	94.71
Gas Carbon Selectivity (%):				
METHANE	39.25	7.14	17.68	14.83
C2+	38.01	59.72	56.70	57.16
HYDROCARBONS	77.26	66.86	74.39	71.99
Total Feed Carbon to Gas Component (Weight %):				
METHANE	26.29	3.92	10.64	8.63
C2+	25.46	32.74	34.13	33.26
HYDROCARBON	51.75	36.66	44.77	41.89
% Coke on Catalyst:	1	1	2	2

The similarities of yields of hydrocarbons from these two feedstocks suggests strongly that the catalytic hydrodeoxygenation reactions occur after thermal pyrolysis, and are solid-gas phase reactions. It follows, therefore, that maximum catalytic activity should be observed generally at the conditions found to be optimal for high yields of pyrolysis compounds in the C_2-C_{10} category.

4.2 Additional Tests - Hydropyrolysis of Poplar Wood in H2 and CO/H2

Wood hydropyrolysis in the presence of a heterogeneous catalyst was attempted in some preliminary tests. These tests were a continuation of the results obtained in earlier studies of catalytic hydrogasification. The major concern of the majority of the hydropyrolysis tests was directed towards conversion by catalytic hydropyrolysis of pure cellulose polymer in order to allow better interpretation of results. The four tests done which gave acceptable data for wood hydropyrolysis are summarized in Table 4.5.

At a later stage of the current project, it was decided to repeat most of the experimentation shown in Table 4.5 to establish, with a greater degree of confidence, an initial database, to evaluate important parameters and to confirm the reliability of the experimental procedure when used by more experienced researchers (initial tests were done mainly by graduate students). In particular, tests A-2 and R-2 shown in Table 4.6 were carried out at the same conditions as Runs 22M and 44M, respectively, as reported previously.

A comparison of these new data with a run (49M) done earlier is shown in Table 4.6, and data in Tables 4.5 and 4.6 can also be compared. Good agreement is evident between

Table 4.5

Initial Tests on Hydropyrolysis of Wood
IEA Aspen Poplar (106-250 μm), ~500°C, 1 atm

Run No.	22M	44M	47M	49M	50M
Atmosphere	Nitrogen	Hydrogen	Hydrogen	Hydrogen	Hydrogen
Catalyst	Sand	C20-6-04	C20-6-04	K499	K502
Support	-	Alumina	Alumina	-	-
Residence Time (s)	0.63	0.59	0.55	0.57	0.57
F/C (g/g h)	0.53	0.50	0.43	0.62	0.33
Feed Rate, g/hour	33.72	21.08	-	26.19	26.32
Yields, wt % maf					
Gas	13.99	42.95	43.71	46.32	46.86
Water	12.17	33.26	34.20	32.04	31.71
Tar	61.11	8.38	8.94	7.80	8.72
Char	14.70	9.93	6.13	14.41	10.74
Total Recovery	101.97	94.52	92.98	100.57	98.03
CO	5.03	13.43	13.31	13.46	12.93
CO_2	6.96	7.09	8.53	7.84	7.09
CH_4	0.34	4.39	3.80	5.58	6.88
C_2H_4	0.15	2.51	2.66	2.08	1.97
C_2H_6	0.04	3.10	2.15	3.39	3.32
C_3H_6	0.07	2.73	2.73	2.65	2.66
C_3H_8	-	0.81	0.55	1.06	0.95
C_4	0.05	2.29	2.37	2.96	2.79
C_4^+	1.36	6.61	7.59	7.31	8.25
Gas Hydrocarbons	2.01	22.44	21.85	25.03	26.82

Table 4.6

Comparison of New and Old Data for Hydropyrolysis of Wood
IEA Poplar, -0.5 mm, 5.4-7.0% moisture, 500°C, 0.5 seconds

Run No.	A-2	R-21	R-22	49M	R-2
Atmosphere	N_2	N_2	H_2/CO	H_2	H_2
Catalyst	Sand	K499	K499	K499	C20-6-04
Feed Rate, g/minute	49.8	56.4	39.0	26.2	36.6
Yields, wt % maf					
Gas	10.8	32.4	54.6*	46.3	44.2
Water	12.2	22.7	26.8	32.0	32.2
Tar	65.7	17.6	8.8	7.8	11.7
Char,coke,soot	7.7	26.3	18.0	14.4	16.4
Total Recovery	96.4	99.0	108.2	100.5	104.5
CO	5.34	13.58	-	13.46	11.47
CO_2	4.78	13.83	36.6*	7.84	4.52
CH_4	0.41	1.84	5.02	5.58	4.13
C_2H_4	0.19	0.46	1.77	2.08	2.40
C_2H_6	-	0.20	1.40	3.39	2.04
C_3H_6	0.09	1.01	2.50	2.65	4.50
C_3H_8	-	-	0.39	1.06	0.71
C_4^+	3.10	1.45	6.92	10.27	14.43
Gas Hydrocarbons	3.79	4.98	34.6	25.03	28.21

* See discussion, CO yield not included

results obtained by different personnel with the same type of equipment but in different laboratories. The total recovery balances for Runs 44M and 47M done previously were too low due apparently to underestimation in "char" yields. This conclusion can be drawn from analysis of data in Table 4.6.

The more recent experiments (designated by prefix A- or R-) shown in Table 4.6 demonstrate the tremendous cracking activity of Katalco 499 catalyst (Run R-21) underlined by the low tar yield of 17.6 wt % with no hydrogen atmosphere present. This high cracking activity leads also to a significant increase in coke or char formation and in gas yield. Most of the additional gas is CO or CO_2 suggesting, in light of the high coke yield, that this catalyst can cause complete decomposition of the thermally generated pyrolysis fragments.

A comparison of nearly duplicate runs, 44M and R-2, shows a much better material balance for the more recent run and a considerably higher yield of C_4+ hydrocarbons and of condensable liquids, the sum of these being 26.1% in R-2 vs. only 17.3% in 44M. This difference is due primarily to more careful experimental and analytical techniques in the later runs. It should be realized that the "tar" reported in these runs is a condensable hydrocarbon liquid, and is

chemically completely different from that formed in uncatalyzed runs such as A-2 or 22M.

Additional experiments compared the behaviour of hydrogen and hydrogen/carbon monoxide mixtures as atmospheres in the catalytic hydropyrolysis. It would be advantageous if synthesis gas could be used in place of H_2. The gas used in Run R-22 had a composition of 48.8% CO and 51.2% H_2 by volume. Yields of CO could not be measured because of the large CO input. However, the excessive yield of CO_2 can only be accounted for by assuming that the Katalco 499 catalyst also catalyzes the reaction

$$2\ CO = C + CO_2$$

At 500°C, the equilibrium for this reaction heavily favors CO_2 production, as was observed. In addition, the char and coke yield (compare Runs R-22, R-2 and 49M) was somewhat higher in R-22 and secondary carbon deposition was more evident in the reactor. It was concluded therefore, that the use of CO/H_2 mixtures would probably not be effective at pyrolysis conditions with catalysts of the type of Katalco 499.

Due to the experimental complications in using CO/H_2 mixtures, particularly carbon deposition on the inlet distributor, it was decided to perform an additional

Table 4.7

Effect of Hydrogen Partial Pressure on Hydropyrolysis of Wood
IEA Poplar, -0.5 mm, 5.4-7.0% moisture, 500°C

Run No.	R-24	R-21	49M	R-22
Atmosphere	H_2/N_2*	N_2	Hydrogen	H_2/CO
Catalyst	K499	K499	K499	K499
Residence Time (s)	0.5	0.5	0.57	0.5
F/C (g/g h)	-	-	0.62	-
Feed Rate, g/hour	23.7	56.4	26.19	39.0
Yields, wt % maf				
Gas	40.20	32.4	46.32	54.6**
Water	36.67	22.7	32.04	26.8
Tar	6.25	17.6	7.80	8.8
Char	5.34			
Coke	6.41	26.3	14.41	18.0
Soot	1.02			
Total Recovery	95.89	99.0	100.57	108.2**
CO	11.86	13.58	13.46	N.D.
CO_2	8.45	13.83	7.84	36.6
CH_4	4.39	1.84	5.58	5.02
C_2H_4	2.17	0.46	2.08	1.77
C_2H_6	2.03	0.20	3.39	1.40
C_3H_6	2.96	1.01	2.65	2.50
C_3H_8		-	1.06	0.35
C_4	2.25	1.45	2.96	6.92
C_4+	6.09		7.31	
Gas Hydrocarbons	19.89	4.96	25.03	17.96

* H_2 to N_2 ratio = 1.25 : 1 by volume

** CO yields not included

N.D. = Not Determined

experiment, but changing the hydrogen partial pressure by dilution with nitrogen. These results are shown in Table 4.7 as Run R-24, together with repeated data of Runs R-21, 49M and R-22 for comparison. From these data, it can be concluded that less than one atmosphere partial pressure of hydrogen diminishes the yield of hydrocarbons (from 25 to 20 wt %), but this yield is still substantially higher than in the case of no hydrogen pressure at all as in Run R-21 in which the hydrocarbon yield was only 4.96 wt %.

4.3 Effect of Pressure on Hydropyrolysis of Wood

Experimental Modifications

The experimental setup put together for hydropyrolysis at elevated pressures is schematically presented in Figure 4.2. To be able to perform experiments at pressures higher than the standard of a few inches of H_2O above atmospheric, the following modifications were implemented:

a) Feeder improvement - an additional oil seal (CP Industries) was put in around the stirrer shaft.

b) Replacement of glass ice-water condensers with a single stainless steel tube 3/8" I.D. x 12" long, with a cold tap water jacket.

c) Replacement of the glass cotton-wool filter holder with a stainless steel filter holder, 1" I.D. x 12" long.

d) Installation of a back pressure regulator (Fischer Model 98L) range 35 to 25 psi, and a pressure indicator.

e) The normal glass U-tube liquid manometers were replaced with two differential pressure transducers (Validyne, Model DP-7, range 0 to 5 psi).

f) New hydrogen rotameter tubes were selected and calibrated for work at 30 psi pressure (207 kPa g).

g) A nitrogen purge was added to the furnace heated volume for additional safety.

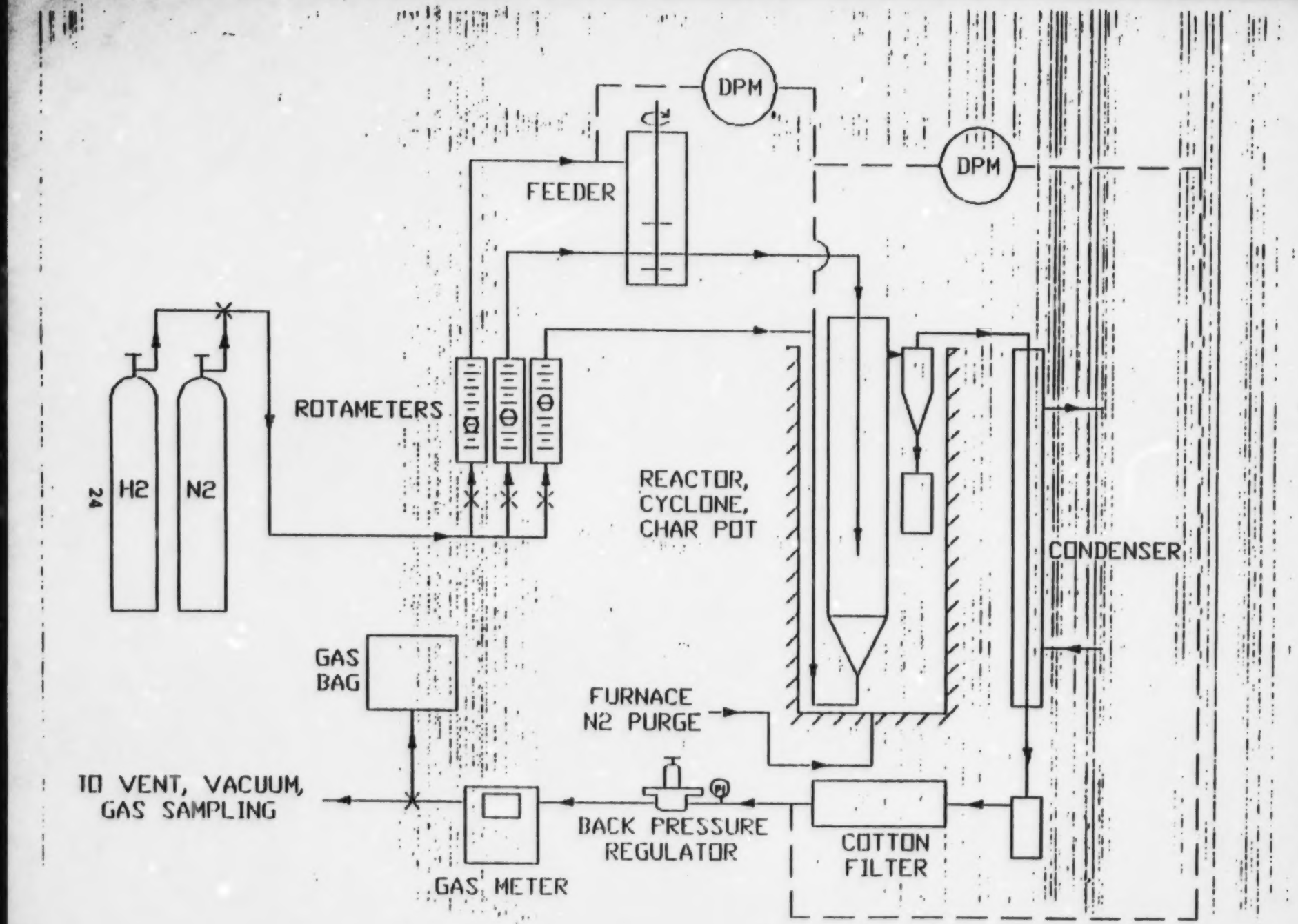


Figure 4.2 Diagram of Bench Scale Fluidized Bed Apparatus Modified for Pressure Operation

The whole system was tested to assure that it was leak proof under pressurized conditions in both N_2 and H_2 atmospheres before actual experimentation was initiated.

Experimental and Analytical Procedures

a) Operating Parameters

Due to limitations of the feeder construction, the working (elevated) pressure was set at 308 kPa abs. (or 44.7 psia, or 3.04 atm).

To have vapour residence times which would still be about 0.5 second, a three times higher mass flow rate of hydrogen was required. Apart from the extensive hydrogen use and the significant dilution of the product gases (which was not beneficial from an analytical perspective), this higher flow rate calls for an increase in the fluid bed catalyst particle size. However, to avoid having to make any major changes in catalyst particle size, it was decided to increase hydrogen flow by only 50% by weight of that used under atmospheric conditions, and to accept the resulting 1.0 second residence time of vapours. Based on these operating criteria, the selected flow rates were; fluid bed - 4.0 liters/min (1 atm, 20°C), and feeder - 5.2 liters/min (1 atm, 20°C).

b) **Experimental Procedure**

Apart from additional gas-leak testing applied under an elevated pressure, the normal routine for bench scale tests established for this laboratory was implemented for data collection.

As usual, the catalyst (when used) was activated in a hydrogen atmosphere at 500°C for one hour. The reactor, feeder, condenser and cotton filter were weighed before and after the experiment to establish the changes in weights. After the run was completed and the apparatus cooled and flushed with nitrogen, the cotton filter and condenser were methanol washed. The amount of water removed with the methanol was measured by Karl-Fischer titration. The amount of water collected with the gases in the form of water vapour was evaluated by gas chromatography using the air-water vapour equilibrium concentration above saturated $MgCl_2$ solution at 20°C as a reference standard.

Gas analysis involved routine gas chromatography. The gas calibration mixture used contained all relevant components. Only the C_4+ fraction was somewhat arbitrarily defined and measured. This fraction included all chromatographic peaks eluting in the range of retention time of butane or longer, but only a butane response factor was implemented in the actual peak area integration.

Because some minor amounts of catalyst were carried over, it was difficult to distinguish between solid products of hydropyrolysis (primary char, secondary char or soot and coke). Very little, if any, catalyst was carried over. Yields of those are reported together as "solids".

Experimental Results

The data for six elevated pressure tests are summarized in Table 4.8. Also included in Table 4.8 are three experiments carried out under normal pressure conditions as a reference and for convenience in drawing some conclusions. Temperatures selected for the tests were in the range 470° to 530°C which is the optimum range for biomass flash pyrolysis having, as a criterium, maximum liquid yield.

Experiments 31 and 32 went exceptionally smoothly producing surprisingly high yields of tar-organics (18 to 22 wt % mf). GC-MS analysis of tar from Run 32 was attempted and results are reported in Table 4.9. The ion count spectra are shown in Figure 4.3 with peaks numbered corresponding to Table 4.9. It is worth noting that peak #28 is the "monomer" of hardwood lignin, and this represents its first reported appearance in pyrolysis products from fast fluidized bed reactors.

Table 4.8

Catalytic Hydropyrolysis of Wood
IEA Poplar, -0.5 mm particle size
Moisture Content 5.5%, Hydrogen Atmosphere

Catalyst: Katalco 499, 30.0 grams (oxide form)

	← elevated pressure →								
Run Number	32	31	30	33	44	42	43	49M	R-8
Temperature, °C	470	504	525	530	487	527	500	500	500
Pressure, psig	30	30	30	30	30	30	0	0	0
" kPa abs	←		303.9			→	←	101.3	→
Feed Rate, g/min	0.39	0.43	0.29	0.39	0.44	0.37	0.49	0.44	0.49
Catalyst Particle Size, mesh	←	-20, +35	→		←	-35, +60	→		Charcoal
" mm		-0.84, +0.50				-0.50, +0.25			-
Yields, wt % mf									
Gas	31.22	35.91	~40	34.8	41.26	45.83	41.84	46.32	49.3
Water	28.00	30.80		41.8	36.64	38.52	27.59	32.04	28.3
Tar	22.62	18.55		7.6	5.53	2.23	7.44	7.80	4.5
Solids	12.65	10.93	16.6		8.67	6.91	12.92	14.41	15.6
Total Recovery	94.49	96.19			91.90	93.49	89.79	100.57	97.7
CO	7.42	8.45	12.5	10.1	11.10	10.47	13.39	13.46	18.16
CO_2	6.23	5.86	6.3	3.9	4.50	3.13	7.30	7.84	8.71
CH_4	2.46	3.63	7.6	7.3	6.35	16.80	4.35	5.58	5.60
C_2H_4	1.25	1.49	1.6	1.0	1.02	0.75	1.84	2.08	1.46
C_2H_6	3.26	3.61	3.6	4.1	5.74	5.92	3.01	3.39	1.95
C_3	0.81	1.04	8.4	8.3	2.92	1.37	3.01	3.71	3.55
*C_4+	9.79	11.83			9.63	7.44	8.94	10.27	9.90

* Mostly vapours of benzene and toluene

Table 4.9

Identification of Peaks in GC-MS Spectra

Peak No.	Name	Match NBS Library	RT (min)
1	2-Butanone, 3-hydroxy	90.3	1.36
2	2-Propanone, 1-hydroxy	97.1	1.51
3	2-3-Pentanedione	93.1	2.48
4	2-Cyclopenten-1-one	94.8	3.29
5	2(3H)-Furanone	88.1	4.09
6	Cyclopropane, methylmethylene	85.0	4.27
7	Cyclohexanone	91.2	4.47
8	No match found (?)		
9	Phenol	94.6	5.24
10	1,2-Cyclopentanedione, 3-methyl	85.7	5.62
11	Phenol, 2-methyl	97.5	5.99
12	Phenol, 3-methyl	98.2	6.18
13	Phenol, 2-ethyl	97.3	6.76
14	Phenol, 2,3-dimethyl	98.9	6.87
15	Benzene, 1-ethenyl-4-ethyl	88.0	7.00
16	Phenol, 3-ethyl	88.5	7.03
17	Naphthalene	91.7	7.26
18	Phenol, 2-propyl	89.7	7.79
19	1H-Indene, 2,3-dihydro-1, 2-dimethyl	87.6	7.98
20	Naphthalene, 2-methyl	98.3	8.21
21	1,4-Methanonaphthalene, 1,4-dihydro	98.0	8.33
22	Phenol, 2,6-dimethoxy	72.8	8.45
23	Naphthalene, 1,3-dimethyl	98.5	9.06
24	Naphthalene, 1,8-dimethyl	85.0	9.16
25	Phenol, 2-methoxy-5-(1-propenyl)	95.4	9.25
26	Levoglucosan, identified by in-house library		9.41
27	2H-1-Benzopyran-3,4-diol, 2-(3,4-dimethoxy)	80.7	9.99
28	Phenol, 2,6-dimethoxy-4-(2-propenyl)	92.4	11.14

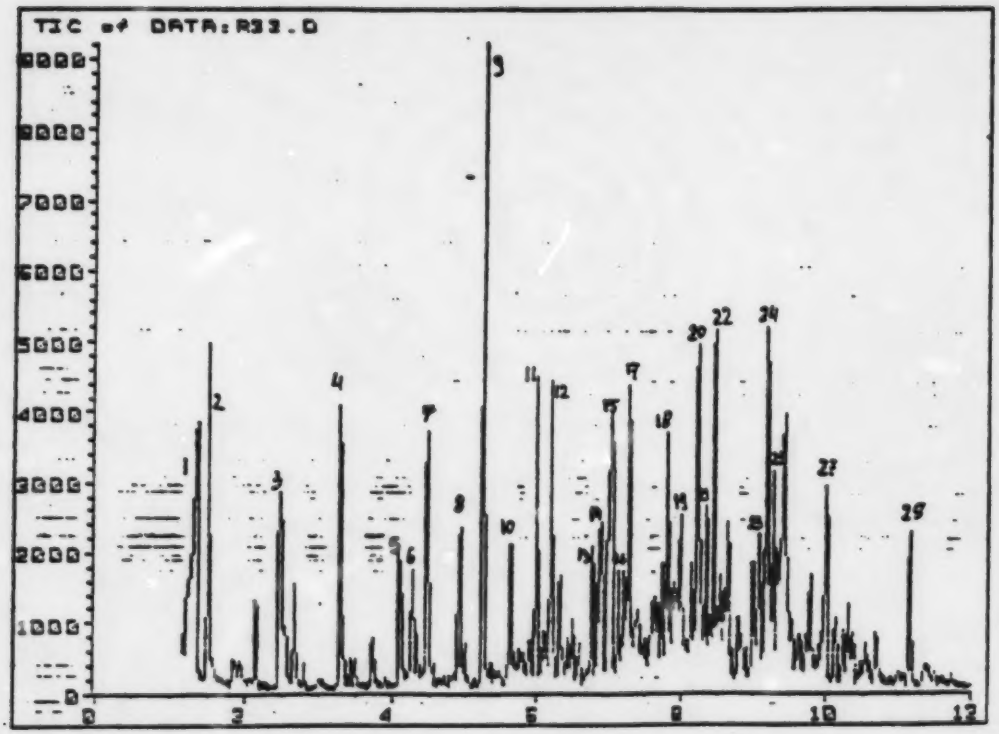


Figure 4.3 GC-MS Spectra of Liquid Fraction (Tar) from Run 32, 470°C, 303.9 kPa abs

Three tests were undertaken at the higher limit of the selected temperature range (above 525°C), Runs 30, 33, 35. During these attempts major difficulties occurred, and only partial results for two runs (Runs 30 and 33) are reported. Operating problems were related in each case to a feeding inconsistency caused by char formation and accumulation in the feeding tube inside the reactor. As a consequence, it was decided to try to use a smaller size of catalyst particles to "loosen-up" the fluid bed somewhat, and to possibly ease the wood sawdust injection delivery.

With the smaller bed particle size, Run 42 went perfectly, yielding a surprisingly low amount of tar (2.2 wt % mf) and indicating a much better catalyst performance. To further evaluate the effect of the smaller size of catalyst particles, an additional test, Run 44, was carried out at ~490°C. The size fraction of Katalco 499 used in Run 42 (-0.50 +0.25 mm) was chosen instead of the -0.84 +50 mm fraction used previously at this range of temperature (Runs 32 and 31).

The low tar yield obtained in Run 44 (5.5 wt % mf) showed again the effect of catalyst particle size, and the importance of contacting between pyrolysis vapours and the catalyst. The results with the finer catalyst particles suggest a higher activity (less tar and more water) with

higher gas yields, and indicate one possible means of controlling the degree of hydrodeoxygenation.

In order to compare the results of catalytic hydropyrolysis under different pressures, Run 43 was carried out at a pressure close to atmospheric. Data for two other tests reported previously using Katalco 499 were also added to Table 4.8, for comparison purposes.

By comparing these data for a single catalyst size, one can judge that an elevated pressure relatively increases methane, ethane and water yields but decreases yields of tar, solids and of both carbon oxides. The yield of carbon dioxide is lower than the value of so-called "prompt" gas, indicating that CO_2 consumption is occurring, possibly by reaction with carbon. This point was addressed in subsequent tests to evaluate hydropyrolysis under elevated pressure in the presence of a catalyst on an activated carbon support.

5. HYDROPYROLYSIS WITH ALTERNATIVE CATALYSTS

5.0 Introduction

Earlier studies on the atmospheric pressure catalytic hydropyrolysis of wood and cellulose have shown that nickel on alumina catalysts are capable of high conversions (70% to 75%) of the carbon in wood to methane. Other catalysts tested, e.g., cobalt-molybdenum catalysts, gave less severe hydrogenation and much larger yields of C_2+ hydrocarbons. However, conversion over these catalysts of carbon to C_2+ hydrocarbons did not exceed about 40%, and some tar and char were also produced, although the tar consisted of heavier hydrocarbons or phenolics.

In this series of tests, an attempt was made to modify the performance of nickel catalysts in two ways, first by using a more neutral support than alumina, and secondly by modifying the cracking activity of the nickel.

In place of alumina, kieselguhr (silica based) was chosen as a support. The agent chosen to modify the cracking activity of nickel was copper. It seems to be reasonably well established that:

a) the surface of massive copper-nickel alloys are enriched in copper relative to the bulk. This appears to be true for supported catalysts as well, provided

that reduction is carried out at moderate temperatures (~770 K)[4].

b) C-O, C-C and C-N bond breaking on nickel requires ensembles of several sites, while a single site is sufficient for hydrogenation [5].

It is therefore hypothesized that the molecular weight, and possibly the oxygen content, of hydrogasified pyrolytic tar, might be enhanced by the use of Ni-Cu catalysts.

5.1 Use of Alternative Catalyst Supports and Additives

Experimental

The feed material used in all tests was standard IEA poplar sawdust, with -0.5 mm particle size and 7% moisture. The analysis of this material, as given in the IEA co-operative analysis project, is:

Extractives	3.0 wt %
Lignin	23.5
Hemicellulose	20.0
Cellulose	49.1
Ash	0.5
	96.1 wt %, dry
Other substances, losses, analytical errors	3.9 wt %
	100.0 wt %
Elemental Analysis-	
Carbon	50.5 wt %, dry
Hydrogen	6.2
Oxygen	43.2
Nitrogen	0.06
Ash	0.4

All tests were carried out in the standard bench scale fluidized bed unit at atmospheric pressure, using the setup and analytical procedures described in previous reports.

General conditions were:

a) hydrogen atmosphere was always used;

b) total pressure was set slightly above atmospheric;

c) temperature in the bed was kept at about 500°C;

d) vapor residence time as calculated for the net reactor volume was about 0.5 second.

Catalysts were prepared using a commercial fluidized bed alumina as support (United catalysts, SAHT-99). Metals were deposited in the usual way by impregnating with aqueous solutions on the nitrates, drying at 110°C and repeating as many times as necessary until the required amount of metal was deposited. Finally, the catalyst was calcined at 550°C for two to three hours to decompose the nitrates [$cu(NO_3)_2$ and $Ni(NO_3)_2$].

The catalysts for Run 3, Run 4 and Run 5 contained:

	Run 3	Run 4	Run 5
wt % Ni	9.0	9.0	9.0
wt % Cu	9.0	0.9	0.09

(These are the calculated weight percents after reduction.)

The origin and description of commercial support material and catalysts used is presented below -

SAHT-99 Alumina powder from United Catalysts Inc.
Louisville, Kentucky
Manufacturer's Data

Al_2O_3	99.5
SiO_2	0.02
Fe_2O_3	0.03
Na_2O	0.45
Porosity	45%
Surface Area	2.60 m^2/g
Pore Volume	0.20 cc/g
Attrition Loss	0.7%
Solid Density	2.00 g/cc
Bulk Density	53 to 60 lbs/cu ft (851 to 963 kg/m^3)
Pore Size Distribution	10 to 0.03 microns

The catalyst for Run 6 was a commercial supported nickel catalyst modified in-house with copper.

Harshaw 0104T 58% Ni on Kieselguhr Impregnated with $Cu(NO_3)_2$ Sufficient to Give 5% Cu
Manufacturer's Data

Chemical Composition	Weight %
Ni	58
Kieselguhr	Balance
ABD (lbs/cu ft)	95
Strength (lbs)	19
Surface Area (m^2/g)	150
Pore Volume (cc/g)	0.20

A hydrogenation catalyst containing 58% nickel on a kieselguhr support. Its rugged activity and versatility make Ni-0104T an ideal catalyst for fixed bed hydrogenation and hydrogenolysis reactions. It may be used in liquid, vapor, or mixed phases. Recommended for hydrogenation of both aromatics and aliphatics.

From: Harshaw/Filtrol Partnership

C20-7-04 Nickel Molybdenum on Alumina
Manufacturer's Data

Chemical Composition	Weight %
NiO	4.0 - 6.0
MoO_3	19.0 - 21.0
P	1.0 - 1.5
Na	<0.05
Al_2O_3	72 - 77
Other Heavy Metals	<0.20
LOI to Constant Weight at 1000°F	<5.0
Bulk Density (lbs/cu ft)	50 ± 3
Surface Area (m^2/g)	150 - 200
Pore Volume (cc/g>29.2 Angstroms)	0.45 - 0.55
Crush Strength, min.avg. (lbs)	20.0

From: United Catalysts Inc.

Results

Summarized data of six tests (one performed at elevated pressure, Run 41) are presented in Table 5.1. Detailed comments concerning individual experiments are given below.

Run 1 Commercial nickel-molybdena on alumina catalyst C20-7-04 was used. The catalyst was crushed and screened to give a particle size fraction of -0.59 +0.30 mm. Condensers were kept at approximately -15°C by using NaCl-ice water solution as a coolant. Soot formation and accumulation was observable in the condensers. A very similar soot formed during an earlier run reported previously (R-2, Table 4.6), and

Table 3.1

Catalytic Hydropyrolysis of Poplar Wood
Catalyst Screening Tests**

Run Number	1	3	4	5	41*	6
Feed Rate, g/min	0.88	1.02	0.81	0.80	0.50	0.87
Catalyst	C20-7-04	9% Nickel on alumina 9.0% Cu	0.9% Cu	0.09% Cu	Same as Run 3	Ni-D104T +5% Cu
Grams	40	50	40	40	38.5	38.1
Yields, wt % mf						
Gas	43.52	20.34	20.74	19.69	22.21	67.87
Water	31.22	12.84	10.85	6.93	14.01	41.28
Tar	12.78	59.62	52.86	54.71	44.87	2.17
Char, coke	5.89	7.03	7.68	8.38	12.09	5.67
Soot	2.43	7.03	5.83	4.05		0.49
Total Recovery	95.83	106.86	97.96	93.76	95.88	117.48
CO	12.39	8.68	8.22	8.86	10.13	1.88
CO_2	6.69	8.56	8.88	7.93	8.53	1.97
CH_4	11.81	0.90	0.85	1.31	1.13	64.02
C_2H_4	0.67	0.16	0.14	0.12	0.19	0.00
C_2H_6	1.72	0.09	0.10	0.08	0.15	0.00
C_3	2.13	0.14	0.10	0.09	tr.	0.00
C_4^+	6.23	1.81	2.46	1.30	4.78	0.00

* Elevated pressure run, 30 psig
** Test conditions given on p 35-36

this soot was sent for elemental analysis to Guelph Laboratories. Results are given below:

Soot from Run R-2

Carbon	65.14
Hydrogen	4.20
Nitrogen	0.33

These numbers seem to suggest that condensation of lignin fragments (free radicals?) may be the source of this soot. Results of this test should be compared with those obtained in experiment 50M (Table 4.5) where a slightly different commercial nickel-molybdena catalyst was used which yielded less methane and more C_2^+ components than shown for Run 1 in Table 5.1 and to Run R-2 where a commercial cobalt-molybdena catalyst was used.

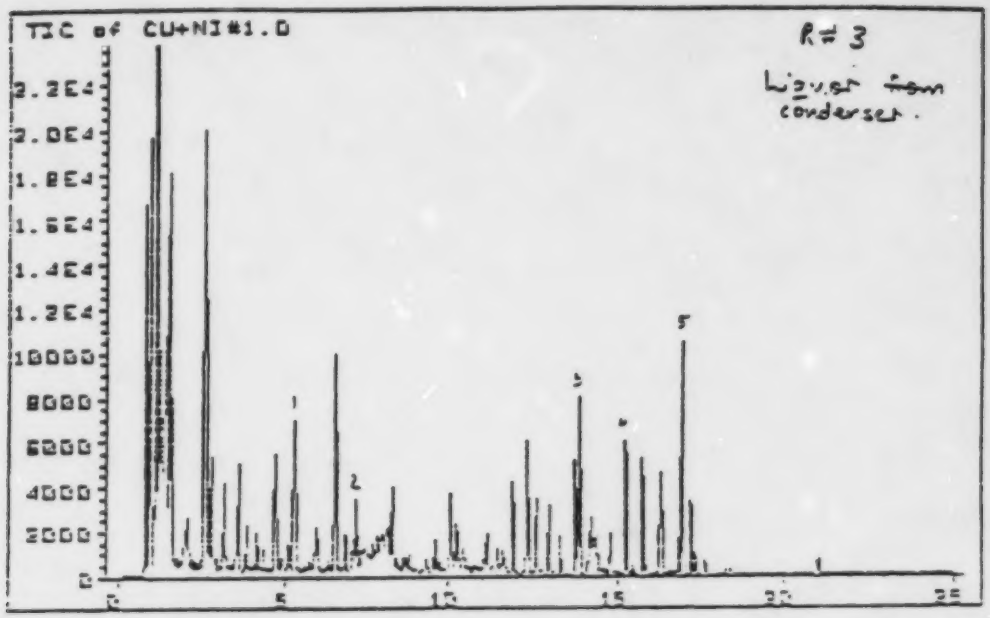
Run 3 Nickel catalyst on alumina modified by copper, with high copper content, made in-house was used. A very high yield of organic tar was obtained (59 wt % mf) suggesting insignificant catalyst activity, if any. Judging from the overall material balance of 106.8 wt % the tar yield may be rather overestimated. Condensables collected at the bottom of the condensers were about 50% of the total liquid product, water

included. This liquid was analyzed by HPLC with the following results:

Water	27.7%	Water Soluble Fraction	
Water Insoluble	9.0	Hydroxyacetaldehyde	16.4
Water Soluble	63.3	Acetic Acid	10.1
		Acetol	6.6
	100.0	Formic Acid	6.5
		Glyoxal	3.2
		Ethylene Glycol	3.0

The presence of carbonyl compounds and the low water yield of 12.8 wt % mf is evidence of the lack of deoxygenation ability of this catalyst.

Run 4, Run 5 - These two runs yielded very similar results to Run 3, although the amount of copper modifier in the catalyst was drastically reduced in each case (see Table 5.1). There was not much difference in the product yields with these three copper-modified catalysts used for Runs 3, 4 and 5. In all cases liquid yields are much higher than from the standard Co-Mo/Al_2O_3 catalyst. A possible explanation may be that on account of the low surface area of this catalyst ($\sim$2.6 $m^2\ g^{-1}$) the specific activity was intrinsically low so that any differences of all three catalysts were obscured by the low activity relative to the biomass loading.



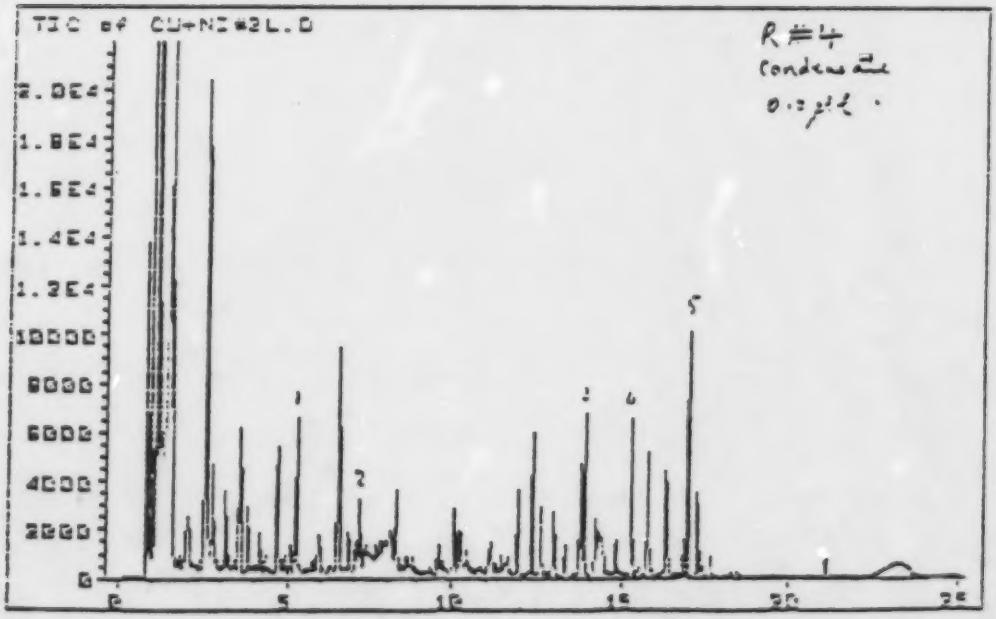


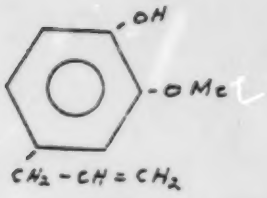
Figure 5.1

GC-MS Chromatographs for Liquid Product
Runs 3 and 4

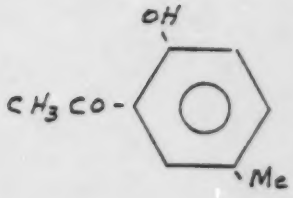
Table 5.2

Identification of Peaks in Chromatograph
of Run 3 and Run 4 Liquid*

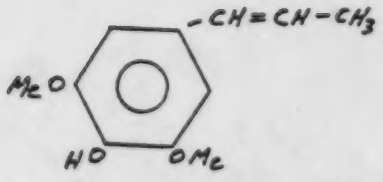
Peak No.	Retention Time (min)	Identification
1	5.20	Cyclohexanone
2	7.15	2-Cyclopenten-1-one, 2-hydroxy-3-methyl
3	13.90	Phenol, 2-methoxyl-4-(1-propenyl)



4	15.30	Ethanone, 1-(2-hydroxy-5-methyl phenyl)



5	17.0	Phenol, 2,6-dimethoxy-4(2-propenyl)



* Done in-house, on our own GC-MS equipment.
Temperature program applied, 50°C for 2 min,
later 10°/min up to 200°C

Figure 5.1 presents the GC-MS total ion chromatographs of liquors from Runs 3 and 4. They are almost identical. Some peaks of interest are identified in Table 5.2.

Elemental analysis of the liquid product from the cold condenser from Run 4 was also done by Guelph Laboratories. Results are shown in Table 5.3

Table 5.3

Elemental Analysis of Liquid Product, Run 4

	As-is	Dry Basis
Carbon	39.16 wt %	54.16 wt %
Hydrogen	8.10	6.95
Nitrogen	0.33	0.46

Run 41 - This run was performed to determine the effect of elevated pressure on hydropyrolysis in the presence of a nickel-on-alumina, copper-modified catalyst. The catalyst from Run 3 (90% Ni, 9% Cu) was used after regeneration. Hydropyrolysis was carried out at a pressure of 30 psig, with a vapour residence time of approximately 1.0 second. The smaller tar yield in Run 41 compared to Run 3 seems to suggest

the possibility of an enhanced hydrocracking ability at higher H_2 pressure. In this run, the total organic liquid product (condenser liquid plus methanol washings of condenser and cotton wool filter) was analyzed by GC-MS. Retention times differ from those in Figure 5.1 because different temperature programming was used. A list of peaks from the total ion count chromatograph tentatively identified is given in Table 5.4.

This list of compounds in Table 5.4 somewhat resembles the composition found for tar obtained in Run 32, performed under elevated pressure which was reported previously. There was no significant BTX found in the gas phase product of Run 41.

Run 6 In this run a high nickel (58%) on kieselguhr commercial catalyst was used (Harshaw Ni-0104T) which had been modified in-house by the addition of 5% copper. A remarkable gas yield (moisture free) of 67.9% was obtained, which was 97.3% CH_4, 1.6% CO and 1.97% CO_2 by volume. This represents a 95.1% conversion of the carbon in the wood to methane - an almost quantitative hydrodeoxygenation.

Table 5.4

Identification of Peaks of Run 41 Liquid Product

Peak No.	Name
1	2-Butanone, 3-hydroxy
2	2-Propanone, 1-hydroxy
3	2,3-Pentenedione
4	2-Cyclopenten-1-one
5	2(3H)-Furanone
7	Cyclohexanone
9	Phenol
10	1,2-Cyclopentanedione, 3-methyl
17	Naphthalene
20	Naphthalene, 2-methyl
22	Phenol, 2,6-dimethoxy
24	Naphthalene, 1,8-dimethyl
27	2H-1-Benzopyran-3,4-diol, 2-(3,4-dimethoxy)
28	Phenol, 2,6-dimethoxy-4-(2-propenyl)

This exceptionally efficient gasification is a marked improvement over our best previous methane yield which represented about 75% carbon conversion. The improved methanation in Run 6 is very likely due to the high nickel content and the neutral support of this catalyst. The copper does not appear to have affected the nature of the catalyst activity significantly, although the char yield is lower for Run 6 (5.7%) than for most other hydrogasification tests using nickel on alumina catalysts (9% to 12%).

This is a single result, and the very high conversion of carbon to methane must be verified. Subsequent work has shown the methane yield to be over-stated for some reason. Later tests with this type of catalyst gave about 55% yield of methane representing a carbon conversion to CH_4 of about 85%. However, the results of Run 6 strongly suggest that it would be worthwhile to repeat Runs 3, 4 and 5 with catalysts based on a neutral high area support material such as kieselguhr.

5.2 Use of Activated Carbon as a Catalyst Support

Introduction

The experimental setup and analytical procedures for operation have already been described. In this series of hydropyrolysis tests, the fluid bed material consisted of particles of activated carbon supplied by Calgon Inc. According to the manufacturer, this carbon is prepared from bituminous coal. Before use, the Calgon activated carbon was ground and screened to obtain the desired particle size fractions.

In tests #39 and #40, activated carbon was the sole material in the bed. All other experiments involved metal catalyst supported by the Calgon activated carbon, which were prepared in-house.

In each test, an amount of 30 grams of selected fluid bed material was put into the reactor. Calculated residence times for tests under elevated pressures were approximately 1.0 second, whereas for normal pressure conditions gas residence times were of the order of 0.5 seconds.

Preparation of Co-Mo/Activated Carbon Catalyst

Activated carbon (Calgon) was crushed and screened. The -20 +35 mesh fraction was impregnated with the active material as follows:

Ammonium molybdate, $(NH_4)_6\ Mo_4O_{24} \cdot 4\ (H_2O44.6\ g)$, was dissolved in a minimal amount of water and sprayed onto 100 g of the carbon while mixing until it became incipiently wet. The carbon was then dried at 110°C and the procedure repeated until the solution was used up;

Cobalt nitrate, $Co\ (NO_3)_2 \cdot 6\ H_2O$ (43.2 g), was dissolved in water and sprayed onto the carbon in a similar manner. At this point the carbon had the light blue tinge typical of Co-Mo oxide. The ammonium nitrate formed was carefully decomposed at 250°C. At this temperature it breaks down to completely volatile products:

$$NH_4NO_3 \text{ -----> } N_2O + 2\ H_2O$$

The loading was chosen so that the weight of Co and Mo per unit volume of bulk carbon was comparable to that of a commercial $Co\text{-}Mo/Al_2O_3$ catalyst containing about 20% MoO_3 and 6% CoO. If the dispersion of the metal, the accessibility of the pores and the volume of catalyst used were the same in both cases, then the number of available active sites would also be the same, thus allowing a more direct comparison of the differences that may be attributable to support effects.

The final composition by mass was

24.7 mass % MoO_3
7.4 mass % CoO

The slightly higher values than the comparable commercial Co-Mo/Al_2O_3 catalyst reflects the lower density of the carbon.

Experimental Results

Data for four tests at elevated pressure using the Co-Mo charcoal catalyst are presented in Table 5.5. One run (37) performed under a "normal" (one atmosphere) pressure condition is also included. Results of Run 8, which was carried out using Calgon charcoal with no added metal, are added to the Table for purposes of comparison.

Some detailed comments about particular experiments are given below.

Run 36 and Run 38 were performed at almost identical conditions. NH_4NO_3 decomposition (part of the preparation of cobalt-molybdena on activated carbon catalyst) for Run 36 took place under nitrogen inside the reactor vessel just before the actual experiment. For Run 38, the final step of catalyst preparation was done in the muffle furnace in the presence of air. Results of the two tests are close, and the minor differences can possibly be attributed to non-ideal gas-solid contacting, since quite a large particle size of activated carbon support was used. The high yield

Table 5.5

Catalytic Hydropyrolysis of Wood
IEA Poplar, -0.5 mm particle size
Moisture Content 5.5% wt
Hydrogen Atmosphere, Elevated Pressure

Catalyst: "Calgon" Activated Carbon

	← elevated pressure →					
Run Number	36	38	39	40	37	R-8
Temperature, °C	490	504	500	500	500	500
Pressure, psig	←		30	→	0	0
" kPa abs	←		303.9	→	102	102
Feed Rate, g/min	0.40	0.37	0.47	0.40	0.44	0.49
Catalyst Particle Size, mesh	-20,+35		-20,+60	-35,+60	-25,+35	
" mm	-0.84,+0.50		-0.84,+0.25	-0.50,+0.25	-0.84,+0.50	
	← CoO/MoO_3 Calgon →		← Calgon →		← CoO/MoO_3 Calgon	Charcoal →
Yields, wt % mf						
Gas	48.77	47.66		43.32	55.78	49.3
Water	47.09	41.31		12.31	34.46	28.3
Tar	0.75	2.77		22.32	5.12	4.5
Solids	2,25	2.36		16.24	7.85	15.6
Total Recovery	98.86	94.10		94.19	103.2	97.7
CO	7.02	6.40	13.32	13.64	20.40	18.16
CO_2	2.05	2.53	9.91	10.06	5.99	8.71
CH_4	28.27	24.02	2.18	2.13	18.41	5.60
C_2H_4	0.33	0.67	0.50	0.45	0.54	1.46
C_2H_6	4.73	4.54	0.77	0.51	3.19	1.95
C_3	tr.	2.59	12.6*	0.53	1.37	3.55
C_4+	6.37	6.91		-16.0*	5.88	9.90

* See detailed comments Run 40 for commentary

of water and the low yields of solids, tar and carbon dioxide, are significant, and indicate that hydrodeoxygenation was efficient on this catalyst, and that coke forming reactions were minimized. From an experimental standpoint, both tests went smoothly.

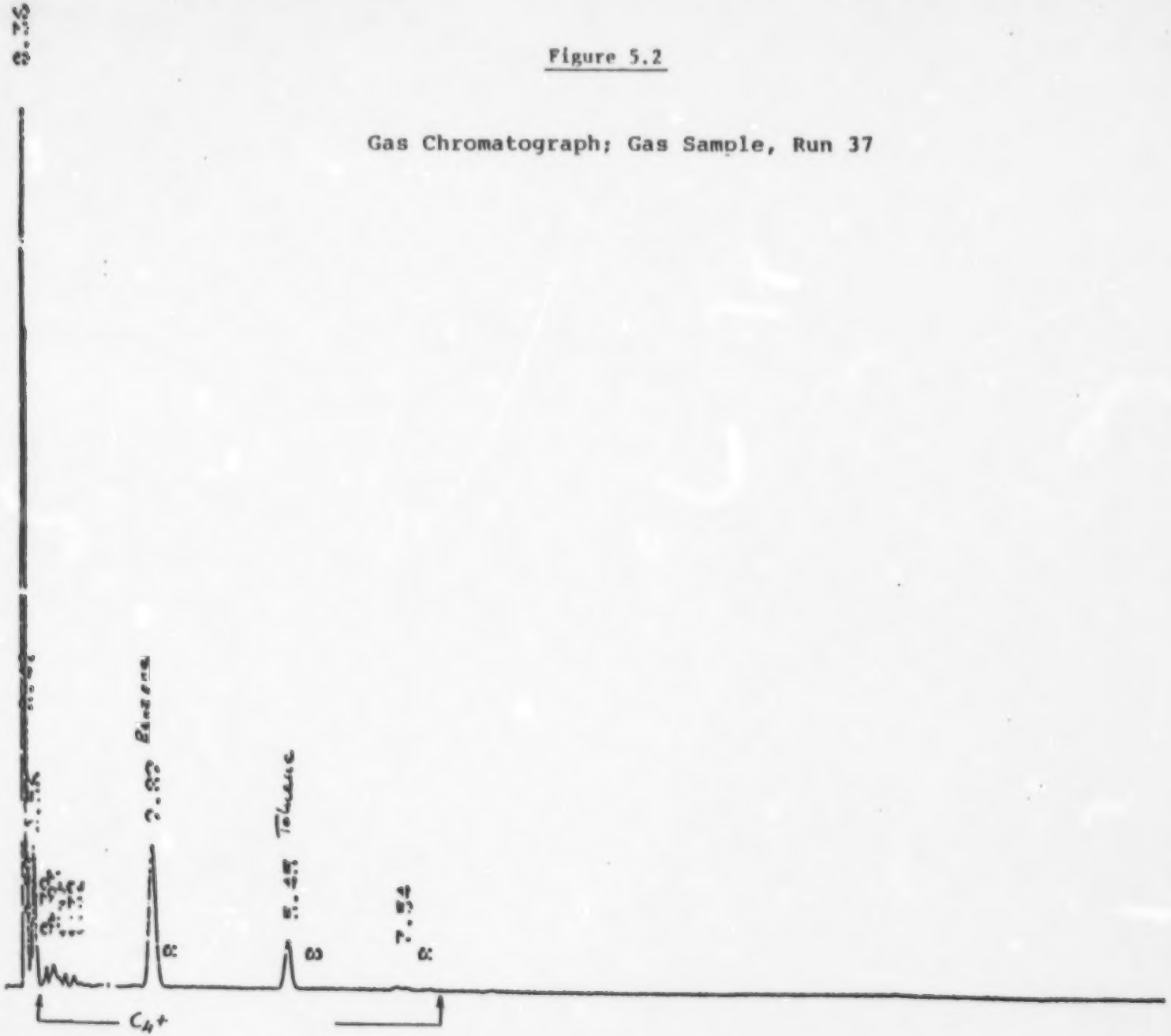
Run 40 was carried out at the same conditions as Run 39. This time the full material balance could be completed. The low water yield of about 12 wt % is typical for flash pyrolysis when no significant hydrogenation is going on. Hydrogenation should not be expected without a metal catalyst present. The cracking ability of the activated carbon is clearly demonstrated by the high gas yield of about 43.3 wt%. For this run, the C_4+ fraction as determined by gas chromatography was calculated using calibration factors related to oxygenated compounds such as formaldehyde, methanol, acetaldehyde, and not those appropriate for pure hydrocarbons.

Run 37 was a very easy test to carry out. It was performed under one atmosphere of hydrogen total pressure using the in-house CoO/MoO_3, an activated carbon catalyst. Comparing the results of this run with a similar one done under an elevated pressure (Runs 36 or 38), yields of water and methane were lower but Co, Co_2, tar and solids yields were higher. These trends must be related to the hydrogen pressure.

In all experiments performed using CoO/MoO_3 on alumina support or on carbon support, the C_4+ fraction contained mainly benzene and toluene vapours as shown in Figure 5.2.

Figure 5.2

Gas Chromatograph; Gas Sample, Run 37



5.3 Use of Kieselguhr as a Catalyst Support

Introduction

In 1985 Scott et al. [1] reported a methane yield of about 55% by weight of the feed obtained during catalytic hydropyrolysis of wood, using a commercial Girdler G-33RS catalyst with a nickel content of 35.6 wt %, on refractory support. In subsequent more detailed investigations [2], it was found that yields of methane using the same Girdler catalyst were only about 45 wt %. Similar values of yield were obtained for methane in tests with in-house made catalyst of nickel content of about 36 wt % [1].

Hydropyrolysis of pure Avicel ph102 cellulose [6] gave methane yields of 46% and 38.4 wt %, using, respectively, nickel and cobalt catalysts supported on kieselguhr. Two typical runs at 500°C done in 1987 are shown in Table 5.6 (Runs 31M and 29M). Also, for an earlier run (Run 6, Table 5.1) we reported a yield of methane of 64 wt % on a dry wood basis, using as a catalyst Harshaw 0104T, 57 wt % of nickel on kieselguhr support, modified by copper. To validate this last very high value it was decided to carry out some additional tests. Three of these (Runs 49, 50 and 51) are discussed in this section, and the results are shown in Table 5.6. In addition, a new catalyst, nickel aluminate, was tested and the results are also shown in Table 5.6 (Runs 59 and 60).

Table 5.6

Catalytic Hydropyrolysis of Poplar Wood

Bench Reactor, 1 Atmos abs

Run Number	49	50	51	6	59	60	Avicel Feed 31M	Avicel Feed 29M
Feed Rate, g/min	0.51	0.65	0.51	0.87	0.46	0.41	0.67	0.73
Temperature, °C	500	500	600	500	500	600	500	500
Catalyst	Ni-0104	Ni-0104	Ni-0104	Ni-0104+Cu	Ni-Alum	Ni-Alum	Ni-0104	G-67RS 54 Co, 2.6 Zr
Catalyst Weight, g	40	40	40	38.1	48	41.5	35.3	39.5
Atmosphere	H_2	N_2	N_2	H_2	N_2	N_2	H_2	H_2
Yields, wt % mf feed								
Gas	59.75	68.04	70.53	67.87	72.23	83.48	52.40	45.25
Water	42.03	3.62	3.47	41.28	-2.95	-4.70	47.35	66.30*
Tar	Tr	7.58	9.28	2.17	5.39	4.60	1.87	5.14
Char, Coke, Soot	5.0	16.10	7.83	6.16	21.40	13.24	2.74	2.83
Recovery	106.78	95.34	91.11	117.48	96.07	96.62	104.35	119.52
H_2 wt % of feed	Tr	3.10	4.32	-	3.56	5.41	-	-
CO	4.15	27.08	48.09	1.88	24.47	58.98	4.16	3.86
CO_2	2.09	29.84	15.64	1.97	37.77	17.54	1.85	2.85
CH_4	53.52	8.02	1.44	64.02*	6.46	1.55	46.24	38.45
C_2H_4			0.34					
Other h.c.			0.7				0.14	0.09

* High

Results

Table 5.6 contains the summarized results of the five new experiments together with some historical data obtained previously in this laboratory, as described in the previous section.

For Runs 49 and 6, which were done at the same conditions except for feed rate, reported yields of water, char and carbon dioxide are identical, within the experimental margin of error. However, the methane yields differ - 54 wt % for Run 49 and 64 wt % in Run 6. The theoretical maximum yield of methane from wood with 49 wt % carbon content should be about 65 wt %. Therefore, a methane yield of 64 wt % as reported in Run 6 is theoretically possible but it should be treated with caution because clearly some carbon remained in the char, tar and carbon oxides and could not be accounted as a source of methane. This suggests that the yield of methane of 54 wt %, obtained in Run 49 should be accepted as a more correct value. Even this lower yield is considerably higher than most yields reported in previous studies, and represents a conversion of feed carbon to methane of 82%, giving a product gas with a composition of 94.5% CH_4, 1.3% CO_2 and 4.2% CO by volume (dry basis).

Reported also in Table 5.6 is an experiment (Run 50) performed in a nitrogen atmosphere at 500°C with the same catalyst batch already used in Run 49. The catalyst was re-activated in a hydrogen atmosphere before the actual nitrogen atmosphere run.

A high total gas yield of 68 wt % was obtained in this experiment, giving a product gas with a composition (dry basis) of 41.9% H_2, 26.2% CO, 18.3% CO_2 and 13.6% CH_4 by volume. On a molar basis, the hydrogen to carbon monoxide ratio in the gas produced was 1.6. The low yield of water of 3.6 wt % indicated the absence of any major dehydration pathway in the catalytic cracking of the pyrolytic vapours originating from the wood, and also shows that the mechanism of catalytic hydropyrolysis is probably an indirect one.

The catalyst from Run 50 was reused to carry out Run 51, again in a nitrogen atmosphere but this time at 600°C. Char-coke yield went down to 7.9 wt % from 16.1 wt % and total gas yield increased to 70.5 wt %. Gas composition changed also with carbon monoxide yield increasing significantly. The product gas (dry basis volume %) had a composition of 49.6% H_2, 39.4% CO, 8.1% CO_2, 2.1% CH_4 and 0.8% C_2+. Compared to Run 50, the hydrogen/carbon monoxide ratio was reduced to 1.26, but the volumetric yield of carbon monoxide and hydrogen increased by a factor of 1.54, due to the re-

duction in CO_2 and CH_4 yields. It is apparent that at the higher temperature of 600°C both CO and H_2 are preferentially produced from the pyrolysis vapours at the expense of char yield primarily. This is also indicated by the reduced yield of methane and carbon dioxide, both products of char formation.

5.4 A New Gasification Catalyst

Introduction

Some early work [7] on the activities and properties of Ni/Al_2O_3 catalysts for the steam reforming of methane suggested that the unreduced catalysts contained nickel aluminate surface phases which on reduction gave a monodispersed form of nickel closely associated with alumina sites as well as Ni crystallites arising from reduction of nickel oxides.

More recent work [8] is in essential agreement with these findings although the precise nature of the monodisperse sites generated by reduction of $NiAl_2O_4$ phases remains unclear. They may be either Ni^+ or Ni^0 as opposed to Ni^{2+} in the unreduced oxide. Most importantly, the evidence suggests that the mono-disperse sites have high stability against deactivation and high activity, at least for steam reforming of methane.

With regard to the stability it may be noted that calcination of 1:1 $Ni:Al_2O_3$ at a sufficiently high temperature leads to the formation of $NiAl_2O_4$ with a spinel crystal structure. It may be that spinels have a particular generic ability to stabilize monodisperse metals for it has also been reported that the copper-alumina spinel $CuAl_2O_4$ shows a similar high activity and stability for the steam reforming

of methanol [9]. In both References [8] and [9] non-stoichiometric catalysts, containing excess Ni and Cu, respectively, were also investigated. It was found that the excess metal was present as a separate oxide phase which generated metal crystallites on reduction. However, under the reaction conditions this free metal was apparently re-oxidized and hence deactivated.

It was also reported in Reference [8] that water dissociation appeared to occur on the same Ni sites responsible for the formation of adsorbed carbonaceous species unlike more conventional supported catalysts for which the acidity of the support seems to play a critical role in activation of water. The presence of only a single kind of monodisperse active site may be helpful towards both activity and stability.

In summary, we decided to explore nickel aluminate spinels as catalysts for biomass gasification because:

(a) Available data suggest that they may possess both high activity and most importantly high stability for reforming of pyrolytic tars. In this context stability is required against carbon deposition, oxidation and sintering.

(b) They represent a more efficient utilization of nickel. For example, stoichiometric $NiAl_2O_4$ contains 33% Ni while the high activity Ni/kieselguhr catalyst (Harshaw Ni-0104) which was tested contained 58% Ni.

Discussion of Results

Two runs (59 and 60) were carried out at 500° and 600°C in a nitrogen atmosphere using a nickel aluminate catalyst prepared by D. Radlein (see Table 5.6). The aluminate was prereduced in flowing hydrogen at the reaction temperature for one hour. For the 600°C run the used catalyst from the 500°C run was reused without any form of reactivation except the prereduction. At the end of both runs the catalyst was of a grey colour and there was little visual evidence of any significant coke/char deposition.

At 500°C slightly more gas and less tar was obtained than over the Ni/kieselguhr catalyst. The gas contained slightly less CO and CH_4 but rather more CO_2. The most noteworthy feature was the very low water yield, in fact, a net consumption of the free water contained in the feedstock was observed. On the other hand, at 600°C a substantially higher total yield of gas (an 18% increase) was obtained as compared to that over Ni/kieselguhr. Furthermore, this gas was richer in both H_2 (25% increase) and CO (22% increase) with a consequent small improvement in the H_2:CO ratio. CO_2

yield was now comparable to that from Ni/kieselguhr. The product gas (83.5% yield) had a molar composition of 51.0% H_2, 39.7% CO, 7.5% CO_2 and 1.8% CH_4.

Tar yields were significantly lower than in the corresponding Ni/kieselguhr runs. This may be an important consideration in any syngas production scheme.

The low water yields are supportive of the suggestion that H_2O is activated on the same sites as the carbonaceous species. When the lowered water and enhanced CO_2 is considered, it seems likely that $NiAl_2O_4$ is an efficient water-gas shift catalyst, more so than Ni/kieselguhr.

If the water-gas shift reaction is being brought to equilibrium then it is possible that the whole system is at thermodynamic equilibrium. Consequently, calculations were made of the expected equilibrium composition based on the overall elemental content. For this purpose the following assumptions were made:

- Wood is taken as $C_6H_9O_4$;
- The whole of the wood reacts with the catalyst. This is clearly not true. We would expect only the pyrolytic tar and gas to be available for reaction. Since the char is relatively richer in carbon, the actual composition of the reactive mass should reflect a relatively

higher hydrogen and oxygen content. However, these calculations are only preliminary and can be improved by using known tar/gas yields and elemental composition;

- Carbon was assumed to be graphite. Again this is certainly untrue. However, the thermodynamic properties of any coke which might form are unknown and it is likely to have a higher free energy (thermodynamically more unstable) than graphite;
- Calculations were made for two temperatures and a variety of reaction conditions. The data clearly indicate that the reaction is not in equilibrium at 500°C but is approaching equilibrium at 600°C with the $NiAl_2O_4$ showing somewhat closer approach than Ni/kieselguhr;
- However, the H_2:CO ratio is higher in the "kinetic gas" at 500°C than in the "thermodynamic gas" at 600°C; 2.05 versus 1.28 for $NiAl_2O_4$ and 1.60 versus 1.25 for the Ni/kieselguhr;
- Comparison of the results for the two catalysts at 600°C indicate that the principal difference is a reduced water yield and enhanced yields of CO and H_2 when using $NiAl_2O_4$. This suggests that the aluminate is an efficient catalyst for the steam gasification of carbon. Presumably this would be the "active carbon"

formed by cracking of the tar on the catalyst. This is a very encouraging sign regarding the potential stability and longevity of the catalyst and is quite in line with our expectations concerning its atomic structure and likely catalytic action. The visual evidence of low carbon deposition on the catalyst is also supportive of this conclusion. On the other hand, the actual yield of solids (char/coke/soot) was higher for the aluminate than for the supported nickel. It seems that further work would be required to clarify this point.

5.5 Screening Tests of Catalysts

Introduction

In summarizing the catalyst testing work on hydrogasification done in our laboratories over the past three years, it involved ten commercial catalysts, three catalyst supports and several laboratory prepared catalysts. These were compared at 500°C, 0.50 to 0.60 seconds residence time and a feed/catalyst ratio (g/g•h) of about 1.00 using the bench scale fluidized bed unit and a hydrogen atmosphere. Fe, Ni, Co, Zn, Cr, Mo, Cu and W were used as metals and silica, alumina, charcoal and magnesia as supports. In many of the tests, Avicel, a pure cellulose, was used as the feed material.

Only a part of the work reported in this Section was within the Contract objectives. A good deal of the research was a part of the fundamental work of graduate students under our direction, and was funded primarily by NSERC. Nevertheless, the results are also included with those obtained while pursuing contract objectives, for the sake of completeness.

Miscellaneous Catalyst Tests - Hydrogasification of Wood

A number of tests with a variety of special catalysts are shown in Table 5.7. These catalysts were selected or

Table 5.7

Catalytic Hydropyrolysis of Wood - IEA Poplar, -0.5 mm, H_2 Atmosphere, 500°C, one atmosphere abs

Run No.	7	9	10	11	14	15	17*	18**	19	13
Feed Rate, g/min	0.68	1.04	0.68	0.65	0.56	0.45	0.70	0.49	0.82	0.62
Catalyst Type	Katalco 499 +Cu	Ni/Co/Mo +Charcoal	Fe/Co/Mo +Charcoal	Co/Mn/K +Charcoal	Cō/Cu +Charcoal	Katalco 494 +30% H_3PO_4	HT300 Harshaw	Ni/Cu +alumina	20% Mo +alumina	Co/Mo +mordenite
Weight, gm	43.1	29.7	39.5	20.8	29.1	36.9	32.9	36.2	51.3	38.8
Yields, wt % m.f. wood										
Gas	44.32	48.25	53.25	36.78	33.25	17.68	39.13	8.95	15.99	29.58
Water	26.34	21.02	25.82	21.30	17.74	10.68	21.69	11.06	13.98	25.63
Tar	16.20	13.25	10.82	16.85	31.79	58.91	20.86	57.40	52.83	28.00
Char, Coke, Soot	13.26	13.87	12.37	19.39	13.99	12.76	17.34	12.94	11.28	14.71
Total Recovery	100.12	96.39	102.26	94.32	96.77	100.03	99.02	90.35	94.08	97.92
Gas Analysis, wt % feed										
CO	11.91	19.54	19.22	16.20	17.52	6.51	11.61	4.41	5.88	9.00
CO_2	10.27	9.44	10.10	12.00	9,06	5.69	9.29	3.52	8.67	8.18
CH_4	4.74	6.39	6.21	3.97	3.04	1.90	4.02	0.56	0.81	3.86
C_2H_4	1.57	1.16	1.71	0.90	0.81	0.43	1.85	0.09	0.30	1.91
C_2H_6	2.20	1.35	2.02	0.49	0.31	0.67	1.48	0.06	0.12	1.06
C_3	3.24	2.40	3.42	1.11	0.95	0.64	2.52	0.09	0.17	1.36
C_4+	10.39	7.47	10.57	2.11	1.56	1.84	6.35	0.04	0.04	4.22

* Residence Time 0.33 sec.

** Feedstock - IEA Poplar washed with H_3PO_4, 0.2% H_3PO_4 added, 465°C, 0.33 sec.

prepared for various reasons, e.g., to reduce cracking while retaining hydrodeoxygenation ability, to reduce degree of hydrogenation to yield alcohol or hydroxy compounds, etc.

The overall conclusion that can be drawn from all of these tests shown is that the earlier results obtained with Co/Mo or Ni/Mo catalysts gave better conversions to hydrocarbons. However, a good deal of information about the probable mechanisms of the direct hydrogasification or hydrodeoxygenation of wood or cellulose was deduced from these results.

A comparison of a number of catalyst formulations with respect to the feed carbon conversion to C_2+ is shown in Figure 5.3 for a pure cellulose feed. The conversions shown include only the volatile fractions appearing in the gas phase and do not include heavier hydrocarbons, phenols, etc., reported as tar. The nature of this tar fraction varied widely depending on the catalyst used. The beneficial effect of molybdenum as a promoter for hydrodeoxygenation is clearly apparent. There is also some evidence that Fe/Mo with Co added (Run 10) may also be a reasonably effective catalyst for hydrocarbon formation. The highest carbon conversions to hydrocarbons (Co/Mo and Ni/Mo on alumina) shown in Figure 5.3 represent largely C_2+ hydrocarbons, with only about 10% to 15% of the C-conversion being to CH_4.

Comparison of Catalysts

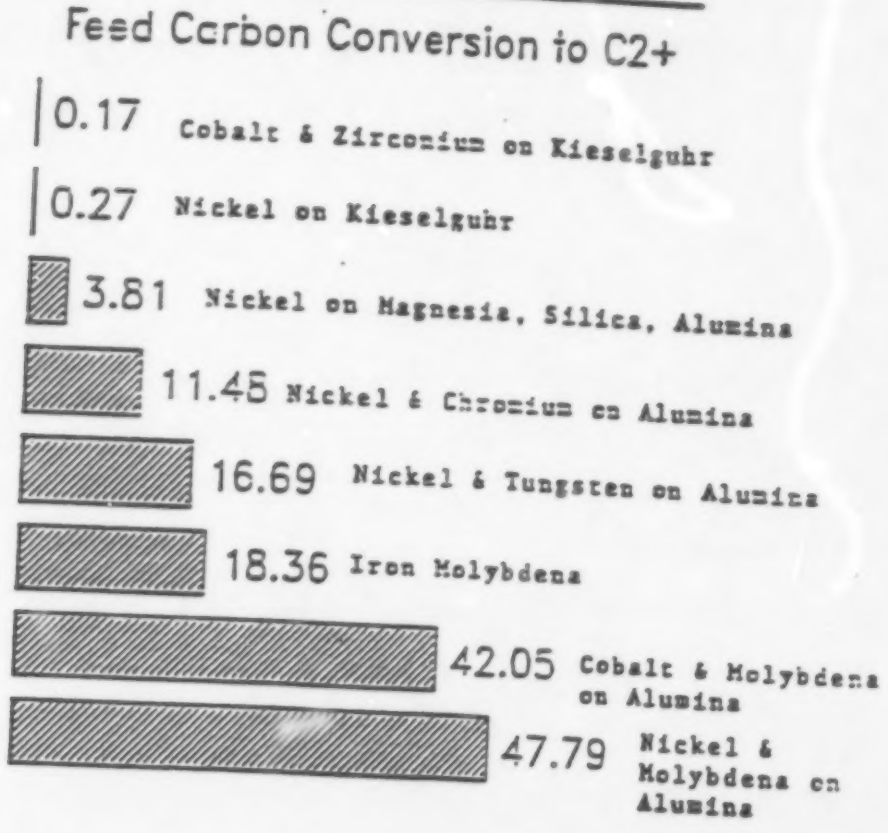


Figure 5.3 Catalyst Screening - Summary of C2+ Results. Carbon coversion to C2+. Hydrogen atmosphere, Avicel PH-102 Cellulose (74-149 μm), 500°C, F/C = 0.61-1.10 g/gh , Average 0.57 s vapour residence time

The tars from two runs giving reasonable yields of this material were analyzed by HPLC (Runs 15 and 18) and the results are given in Table 5.8. The addition of phosphoric acid to the catalyst resulted in a tar high in hydroxyacetaldehyde. Conversely, when the wood was treated with phosphoric acid, a high yield of levoglucosan was obtained. In both cases, the yield of pyrolytic lignin was sharply reduced.

Use of a Size Selective Support (Zeolite)

In order to evaluate whether a size selective (zeolite-type) material used as a support for a Co/Mo catalyst would give more selective results, particularly in increasing aromatic yields, one test was carried out with this type of catalyst prepared in-house (by D. Radlein). A medium pore zeolite, H-mordenite (Zeolon 900H, Norton Co.) was used as it was felt that the best chance of observing a "zeolite" effect would be with a large pore material allowing relatively rapid intra-pore diffusion. The effective pore diameter of the mordenite was given as 8-9°A with a crystalline void volume of 0.28 cm^3/cm^3.

To allow for comparison of results with the standard hydrotreating Co/Mo catalyst, the mordenite was impregnated with approximately the same amounts of metal. The final

Table 5.8

Analysis of Tar Fraction by HPLC, Yields wt %, m.f. Wood

Run No.	15	18
Oligosaccharides	tr	tr
Cellobiosan	0.39	0.94
Glucose	tr	0.45
Fructose	tr	0.61
Glyoxal	0.88	0.69
1,6-Anhydroglucofuranose	tr	1.25
Levoglucosan	1.17	9.75
Hydroxyacetaldehyde	11.50	2.31
Formic Acid	2.72	tr
Formaldehyde	1.16	tr
Acetic Acid	2.59	1.28
Ethylene Glycol	0.38	tr
Acetol	1.92	1.04
"Lignin"	13.57	17.09

catalyst contained, before reduction, about 6% CoO and 19% MoO_3.

The results of the hydropyrolysis tests are shown in the general table of results (Table 5.7) as Run 13. Conversion to gas was relatively low (30%) and the tar product was high at 28%. These values can be compared to 44% and 13%, respectively, for the standard Co/Mo on alumina hydrotreating catalyst. Water production was high at 26% indicating some typical dehydration activity by the zeolite, especially because a more than usual amount of secondary carbon (soot) also formed. As strong acid zeolites are powerful cracking catalysts that favour dehydration reactions, and the impregnation method for Co-Mo retains this acidity (as opposed to metal addition by ion exchange), then some dehydration activity would be expected.

The gas analysis shows a higher than usual CO_2 production. This result, coupled with the high water yield and reduced yield of C_2+ hydrocarbons, suggests a reduced oxygen content of the tar and char. One possible explanation of these results may be that most of the Co-Mo component is contained within the intercrystalline voids of the zeolite and is therefore not readily accessible to the pyrolysis vapours, or in effect, intra-crystalline diffusion is slow

compared to the gas velocity. This effect was probably exacerbated by the relatively large particle size of the zeolite (0.30 to 0.84 mm).

For improved results with a zeolite-based catalyst, smaller particle sizes and different methods of depositing metals should probably be used.

6. THERMOCATALYSIS USING AN H-DONOR

The objective of this set of tests was to carry out co-pyrolysis of biomass and a hydrocarbon feedstock, in this case poplar wood sawdust and propane in both a non-catalytic and a catalytic fluid bed. It was hoped that the very high molar heat capacity of propane would allow the pyrolysis of wood at lower temperatures than those presently found to be optimal (500°C) for maximum liquid yield, but with roughly the same yield of total volatiles. Also, if there is any possibility of free radical interaction-recombination, or coupling, some evidence of it should be detectable in the final mixture product spectra, given the ease with which free radicals can be formed thermally from propane. It was also a possibility that greater catalytic activity and longer life might result from the lower temperature operation.

Runs AL-12 and R-23, shown in Table 6.1, were carried out at 475°C and 450°C, using a propane-nitrogen mixture of 5.8 : 1 by volume. The low char yield of 6.8 wt % in Run AL-12 proved that the first concept of lowering the optimum temperature in uncatalyzed thermal pyrolysis was probably valid, since pyrolysis in nitrogen at 500°C yielded char in the 8 to 14 wt % range, approximately comparable to that in N_2/propane at 475°C.

Table 5.1

Effect of Added Hydrocarbon on Catalytic Pyrolysis of Wood
IEA Poplar, one atmosphere pressure, -5.5 mm particle size

Run No.	AL-12	R-23	R-21
Moisture Content, wt %	5.5	5.5	5.4
Temperature, °C	475	450	500
Atmosphere	Propane/N_2	Propane/N_2	Nitrogen
Catalyst	Ottawa Sand	K499	K499
Residence Time (s)	0.43	0.45	0.60
Feed Rate, g/minute	0.53	0.51	0.94
Yields, wt % mf			
Gas	11.12	29.63	32.40
Water	13.09	30.17	22.70
Tar	65.06	15.38	17.60
Char	6.80	12.92	7.16
Coke	-	17.23	18.36
Soot	-	0.62	0.72
Total Recovery	96.37	105.95	98.94
CO	5.08	10.61	13.58
CO_2	6.04	12.57	13.83
CH_4	N.A.	1.20	1.84
C_2H_4	-	0.76	0.46
C_2H_6	-	1.62	0.20
C_3H_6	-	N.A.	1.01
C_3H_8	-	N.A.	-
C_4^+	-	2.87	1.45
Cellobiosan	0.73		
Glyoxal	0.97		
Levoglucosan	2.98		
Hydroxyacetaldehyde	8.25		
Acetic Acid	2.32		

This possibility of lowering the optimal pyrolysis temperature may be applicable in the thermal production of anhydrosugars from pretreated wood, where a temperature lower than 500°C could be beneficial in preserving the molecular structure of the anhydrosugars formed.

The yields of gases shown by a comparison of the catalytic Runs R-21 in nitrogen, R-23 in nitrogen-propane and 49M in hydrogen show that the propane is not acting as a hydrogen donor as had been hoped. In fact, hydrocarbon yields over the catalyst in a nitrogen-propane atmosphere are very similar to those obtained in pure nitrogen alone, although at a temperature 50°C lower. However, as mentioned previously, this lowering of the pyrolysis temperature is thought to be due to the high heat capacity of the propane.

7. PYROLYSIS OF STARCH AND GRAIN

7.1 Thermal Pyrolysis of Corn Starch and Corn Grains

Pyrolysis of Corn Starch

A series of three experiments were performed in the bench scale fluidized bed unit using Saint Lawrence Pearl "C" starch as a feedstock for pyrolysis. Temperatures of the reaction were 460°, 515° and 555°C. The experimental procedure was the same as for pyrolysis of lignocellulose biomass. The corn starch was first screened and a uniform size fraction used as the feed.

The operation of the equipment was more difficult than for normal biomass experiments and somewhat resembled the pyrolysis of acid-washed wood. There were problems with feeding due to the low softening temperature, and at the lowest temperature (460°C) the fluidizing bed was agglomerated by the pyrolysis products. At higher temperatures, no agglomeration of the fluidizing sand was observed.

The feeding of the reactor tended to occur in pulses, apparently because some pyrolysis product was formed in the feeding tube inside the reactor which was later blown out, due to the increase of pressure in the feeding line. Then the cycle of accumulation in the feeding tube, accompanied by pressure increase, was repeated. Usually each feed cycle lasted for about 1.5 to 2 minutes. Because of a relatively

high pressure which developed in the feeding line, the feed rate which was planned to be 30 to 40 g/h, actually was three times greater.

The operating conditions of the experiments and the product distribution are presented in Table 7.1. Very little char was collected in the char pot and most of it stayed in the bed or in the outlet tube, similar to the behaviour of acid-washed wood. The yield of gas was low while the yield of liquid product was 70% to 80%. This liquid product contained the same components as obtained from cellulose pyrolysis tar but in different proportions. The amount of the water-insoluble part of the liquid was surprisingly high, as compared to that found in similar pyrolysis tars from cellulose. The main components of the water-soluble part of tar were levoglucosan and hydroxyacetaldehyde. The compositions of tars from the three runs are shown in Table 7.2. The K-F water determination was difficult for these tars, so water content is approximate.

It can be concluded that fast pyrolysis of starch can be successfully performed at temperatures above 500°C yielding a high amount of liquid product containing substantial amounts of both levoglucosan and hydroxyacetaldehyde. A significant yield of water-insoluble liquid product is also

Table 7.1

Pyrolysis of Corn Starch

0.5 seconds, N_2, atmospheric pressure

Run Number	St #1	St #2	St #3
Temperature, °C	460 ±20	515	550
App. Res. Time, s	0.5	0.5	0.5
Feed Rate, g/h	100.4	89.4	139.3
Amount Fed, g	24.3	37.3	55.7
Moisture, w/w %	7.9	7.9	7.9
Particle Size, mm	-0.59 +0.3	-0.59 +0.3	-0.59 +0.3
Yields, w/w % m.f. feed			
Gas	3.1	5.7	5.1
Char	11.5*	1.9*	1.5
Water	8.1	6.0	9.6
Organic Liquid	70.8	81.2	75.1
Total	93.5	94.8	91.3
CO	1.0	3.7	3.8
CO_2	2.1	2.0	1.2
CH_4	tr	tr	tr
C_2H_4	n.d.	n.d.	n.d.
C_2H_6	n.d.	n.d.	n.d.
C_3H_6	n.d.	n.d.	n.d.
C_4H_{10}	n.d.	n.d.	n.d.
Levoglucosan	19.8	14.4	12.2
Hydroxyacetaldehyde	4.0	12.5	12.0
Water-Insoluble	15.3	13.0	20.0

* Char was mainly accumulated in the fluid bed
n.d. - not detected

Table 7.2

Composition of Tars from Pyrolysis of Corn Starch

HPLC of Total Liquid Product

Run No.	Tar w/w % St #1	St #2	St #3
Compound Name			
Oligosaccharides	0.62	0.60	0.34
Cellobiosan	3.09	5.74	4.51
Glucose	Trace	-	Trace
Fructose (?)	1.18	1.54	1.62
Glyoxal	Trace	2.55	2.30
1,6 Anhydroglucofuranose	3.09	0.95	0.30
Levoglucosan	25.00	16.58	15.85
Hydroxyacetaldehyde	5.11	14.45	15.37
Formic Acid	-	-	-
Formaldehyde	-	-	-
Acetic Acid	-	-	-
Ethylene Glycol	-	-	-
Acetol	-	-	-
Methanol (Solvent)	9.92	14.00	9.58
Eluted Identified	48.01	56.41	49.67
Eluted Unidentified	3.70	4.50	3.64
Water Insolubles	19.40	15.00	25.80

obtained, but the character of this material is as yet unknown.

Pyrolysis of Corn Kernels

Whole grains of corn were ground, and a fraction -30 +50 mesh was selected as a feedstock for fast pyrolysis in the bench scale unit. Two experiments were performed, at 470° and 425°C. Experimental conditions used and product distributions obtained are presented in Table 7.3. The yields of organic liquid products were about 65%, which is similar to other biomass materials. However, this liquid contained more unidentified components (by our standard HPLC analytical methods) and had an unpleasant smell resembling products of protein decomposition.

Pyrolysis of corn grains was more trouble-free than that of corn starch, but did not supply any single product component in a greater amount. The results of the HPLC analyses of the whole tar fraction are given in Table 7.4. The lower temperature of 420°C gave a much better yield of sugars than did the test at 470°C, in agreement with the results from corn starch, which also gave the highest yield of sugars at the lowest temperature.

Table 7.3

Pyrolysis of Corn Kernels

Atmospheric pressure, N_2

Run Number	C 1	C 2
Temperature, °C	470	425
App. Res. Time, s	0.5	0.5
Feed Rate, g/h	46.6	44.5
Amount Fed, g	25.6	18.6
Moisture, w/w %	1.9	1.9
Particle Size, mm	-0.59 +0.3	-0.59 +0.3
Yields, w/w % m.f. feed		
Gas	9.2	6.6
Char	7.8	17.2
Water	11.5	8.3
Organic Liquid	64.2	65.6
Total	92.7	97.7
CO	3.7	1.3
CO_2	5.5	5.4
CH_4	traces	traces
C_2H_4		
C_2H_6		
C_3H_6		
C_4H_{10}		
Levoglucosan	6.5	9.9
Hydroxyacetaldehyde	4.7	3.9
Acetic Acid	0.5	0.8
Acetol	-	-
Water-Insoluble	10.5	8.0

Table 7.4

HPLC Analyses of Liquid Product from Corn Kernels

Run No.	Tar w/w %	
	C 1	C 2
Compound Name		
Oligosaccharides	-	-
Cellobiosan	2.33	3.57
Glucose	-	-
Fructose	-	0.62
Glyoxal	1.48	1.41
1,6 Anhydroglucofuranose	0.91	1.96
Levoglucosan	10.17	15.05
Hydroxyacetaldehyde	7.38	5.98
Formic Acid	-	Trace
Formaldehyde	-	Trace
Acetic Acid	0.71	1.26
Ethylene Glycol	-	-
Acetol	-	-
Methanol (Solvent)	8.63	6.91
Ethanol (Solvent)	15.67	9.99
Eluted Identified	47.28	46.75
Eluted Unidentified	1.30	2.60
Water-Insolubles	16.30	12.20

7.2 Catalytic Hydrogasification of Starch

Preliminary Tests

Inasmuch as no previous experience existed to guide the selection of optimum fast pyrolysis conditions for starch to obtain maximum hydrocarbon yields via catalytic hydropyrolysis, some preliminary tests and a literature review were carried out. The results of this preliminary work are summarized below.

a) Samples used

1) Starch powder - ordinary food grade corn starch powder from corn as sold in supermarkets (Best Foods Canada Inc.). Moisture 9.1%.
2) Pearl "C" starch - a granulated starch obtained from St. Lawrence Starch Co. Ltd. Grain size was about -6 +60 mesh. Grains were structurally weak. Properties are given in Appendix 1 (starch powder tested in 1) above was essentially the same product except for particle size).
3) Corn kernels - field corn kernels (Waterloo County) ground and screened to -0.5 +0.3 mm. Moisture content 2.0% by weight.
4) Soft wheat hearts (semolina) - standard supermarket flour.
5) Avicel 102 microcrystalline cellulose.

b) A review of the literature yielded pyrolysis-mass spectrometry spectra for amylose and for cellulose, of the type normally generated for analytical purposes. These spectra and the authors' comments are shown as Figure 7.1 [10].

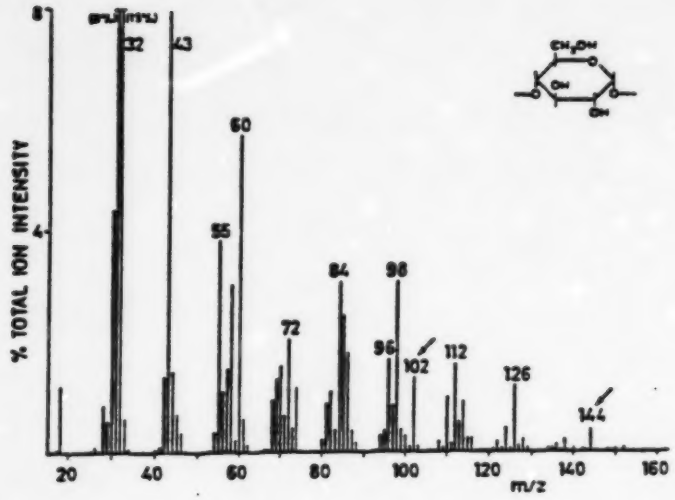
c) "Hot plate" visual observations

Recently we have observed that the melting/charring behaviour of biomaterials when dropped on a hot plate can give useful preliminary information about their behaviour in a fast pyrolysis reactor. Accordingly, all the starches used in this work were examined in this way by dropping on a hot plate surface held at approximately 500°C.

In all cases; (i) particles of starch melted on contact with the hot plate yielding a gummy viscous black boiling liquid, (ii) tar-fog evolution was visible and rapid, (iii) a solid single mass of refractory char-coke remained as a final product.

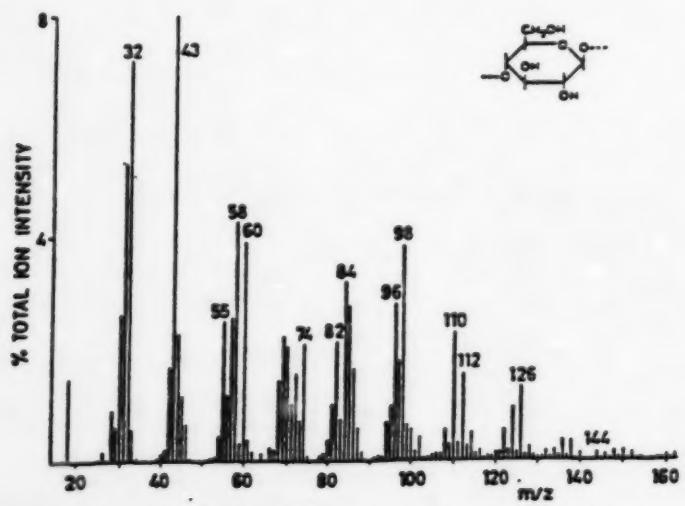
d) Thermogravimetry

Thermogravimetric analyses of three samples were carried out - corn starch powder, corn kernels and Avicel 102. The conditions of the experiments are listed below.



SAMPLE	: AMYLOSE
CHEMICAL DETAILS	: poly[(1→4)DGlc$_p$]; see insert in spectrum
SAMPLE ORIGIN	: Merck AG, Darmstadt, GFR
SAMPLE PREP./SIZE	: suspension in methanol; 10 µg
PYROL. CONDITIONS	: standard
TOTAL ION COUNTS	: 1 X 10^5

REMARKS - Note the relatively high peak intensities at m/z 55, 72, 102 and 144, and the relatively low intensities at m/z 58, 74, 82, 96, 110 and 124 compared with the spectra of the β(1→4)-linked analogue (Spectra A.1 and A.1a). Similar characteristic differences are exhibited by the other glucans containing α-glycosidic linkages (Spectra A.3 and A.4).



SAMPLE	: CELLULOSE
CHEMICAL DETAILS	: poly[(1→4)DGlc$_p$]; see insert in spectrum
SAMPLE ORIGIN	: Whatman Chromedia, W.& R. Balston Ltd., UK
SAMPLE PREP./SIZE	: suspension in methanol; 10 µg
PYROL. CONDITIONS	: standard
TOTAL ION COUNTS	: 2.8 X 10^5

REMARKS - Note the high degree of correspondence with Spectrum A.1. As demonstrated by Meijman (ref. 169), well purified celluloses from widely different origins (e.g. cotton wool, fungal cell walls) exhibit identical Py-MS patterns.

Figure 7.1
Pyrolysis Mass Spectra
for Amylose and Cellulose
Reference 10

Equipment : Perkin-Elmer TGS-2 Thermogravimetric Analyzer

Atmosphere : Nitrogen

Sample Size : 3.5 to 7.0 mg

Program Used : Initial temperature of 100°C held as long as weight loss due to water removal was visible followed by a ramp rate of 50°/min applied up to the final temperature of 600°C.

Results of these tests are shown in Figures 7.2 and 7.3 in which corn starch and corn kernels are compared (Figure 7.2) and corn starch and cellulose are compared (Figure 7.3). It is apparent, as would be expected, that starch decomposes in a much narrower temperature range than does corn, while starch decomposes at a lower temperature and with more residue than does cellulose. Some key values from these plots are given in Table 7.5.

Table 7.5

Key Values from Thermogravimetric Analysis

	Temperature, °C of Initial 10% Weight Loss	Final Residue at 600°C Weight % of Initial Dry Sample
Field Corn	317	17.8
Corn Starch Powder	342	9.5
Cellulose (Avicel)	366	3.3

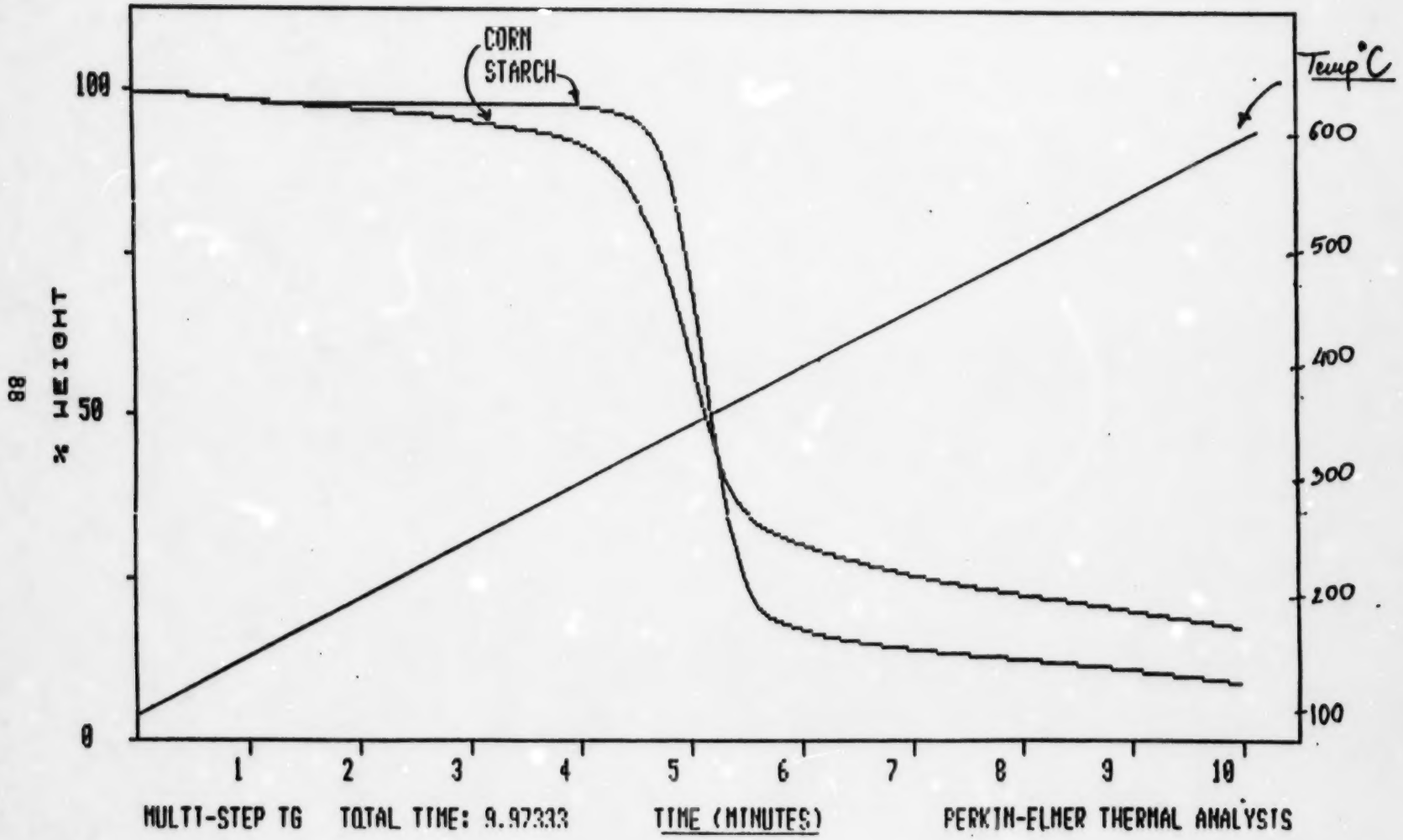


Figure 7.2 TGA Results for Corn Kernels and for Corn Starch

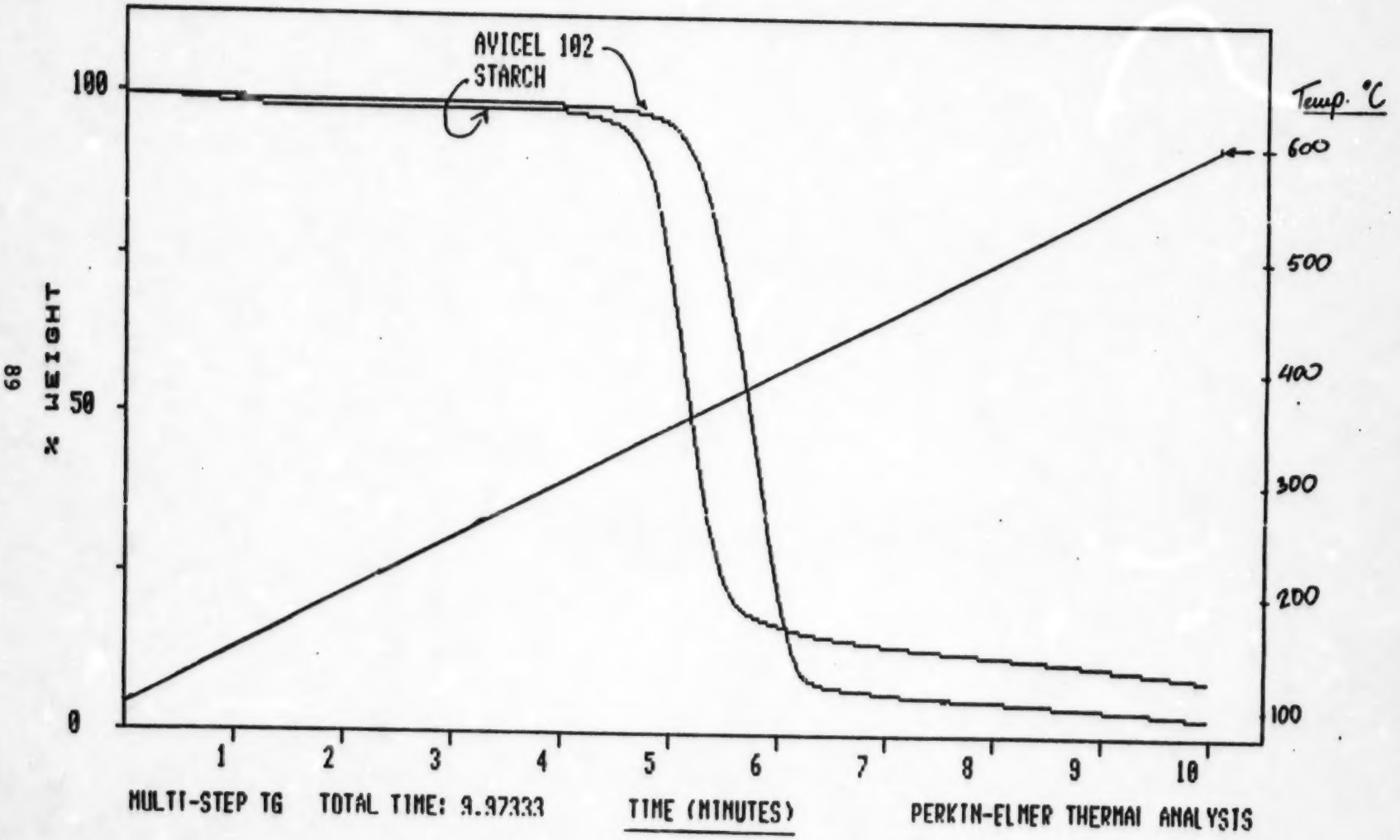


Figure 7.3 TGA Results for Corn Starch and Avicel 102 Cellulose

Bench Scale Hydrogasification Tests

Unless otherwise stated, all pyrolysis tests were carried out in the bench scale fluidized bed unit at atmospheric pressure with an atmosphere of 100% hydrogen at approximately 500°C.

A) Pyrolysis of Corn Starch Powder (9.1% moisture)

Catalysts used i) Katalco 499

ii) C-20-6-04 (United Catalyst Inc.)

In all tests, catalysts were reduced in H_2 atmosphere at 500°C prior to the start of the feed.

Three attempts were made to carry out pyrolysis experiments using the above catalysts, but all failed due to the powdery nature of the solid starch. Feeder modifications (changing orifice diameter from 1.3 mm to 1.0 mm and next to 0.6 mm) did not eliminate the erratic feed delivery. Because of this feeding problem, the experiments were terminated after a few minutes. Visual observation of the fluid bed after cool-down indicated a coke-char build-up inside the reactor, and the particles of catalyst were agglomerated to some degree.

It was decided to change to a feedstock with a more suitable particle size distribution.

B) Pyrolysis of Field Corn (2.0% moisture)

Catalyst used - C-20-6-04 (United Catalyst Inc.)

Kernels of field corn were dried, ground and screened, which was a very tedious sequence of operations due to the oily character of the corn itself. A very narrow particle size fraction (-0.5 +0.3 mm) was selected to secure a good feeder performance. Satisfactory feeder performance was proven in cold tests.

Hydrogasification attempts were carried out using a modified version of the inlet feeding tube. A central tube carried the corn particles from the feeder in a stream of hydrogen. An auxiliary hydrogen stream flowed in the annulus of a surrounding tube and introduced additional agitation of the fluid bed at the feed entrance point to help prevent agglomeration. Attempts to accomplish a quantitative pyrolysis run were never completed to a degree which would allow a satisfactory detailed material balance and product analyses. In every test, melted starch plugged the feeding line causing early termination of the experiment.

C) Pyrolysis of Semolina (wheat flour)

Catalyst used - COMO-0401 (Harshaw Chemical Co. - cobalt-molybdenum on alumina)

Although this feedstock demonstrated the best performance of the feeder of all the starches tried, the actual pyrolysis experiments failed. Again, the feeding tube plugged at the exit point. The char plug formed could only be cleaned off by burning with a Bunsen burner.

D) Pyrolysis of Granulated "Pearl" Starch (St. Lawrence Starch Co.; 9% moisture)

Particles of this starch were very fragile, and the particle sizes given above should be treated as indicative only of the initial material placed in the feeder.

An air cooled feeding tube arrangement was put in place of the former feed tube used for corn and semolina. A hydrogen stream with starch particles from the feeder flowed in the central feed tube which was surrounded by a jacket through which cooling air was circulated.

Two hydrogasification tests were carried out which yielded data. Feeding in both cases was very irregular with the feeder itself working to some extent as a powder generator due to the fragility of the starch particulates.

Plugging of the feed tube and agglomeration of the bed solids persisted but to a lesser degree than in the case of powdered starch. Some overall results were obtained, and are given in Table 7.6 as Runs 28 and 29. Some results using a pure cellulose (Avicel 102) are also shown as Run 42M done under the same conditions, for comparison.

Hydrocarbon gases (C_1 to C_3) represented 1.8% and 3.7% of the feed, in Runs 28 and 29, respectively, while C_4+ volatiles were 4.7% and 5.4%. The liquid product composition is unknown, but a rough oxygen balance indicates that it contains about 20% oxygen. CO and CO_2 yields are higher than expected.

In general, the results are not particularly encouraging when compared to the yields obtained from the catalytic hydrogasification of wood or cellulose. As a general conclusion, the fluidized bed reactor does not appear to be particularly suitable for high starch content materials because of their low melting point, which causes agglomeration of the bed. It is possible that a modified reactor design specifically engineered for these materials might give better results.

Table 7.6

Pyrolysis of Pearl Corn Starch

Run Number	28	29	42M *
Atmosphere	Hydrogen	Hydrogen	Hydrogen
Catalyst	COMO-0401 reduced	C-20-6-04 reduced	C-20-6-04 reduced
Feed Rate, g/hr	171	44	46.1
Temperature, °C	500-550	510-550	495
Yields, wt %, m.f. feed			
Gases	23.8	22.4	42.0
Water	27.5	- 20	38.6
Organics	31.5	39.6	7.7
Char-coke	12.3	12.6	4.1
	95.1	94.6	92.4
Gas Composition, wt % m.f. feed			
CO	10.0	7.2	13.0
CO_2	7.4	6.1	9.3
CH_4	0.6	1.6	2.3
C_2H_4	0.35	0.7	1.7
C_2H_6	0.20	0.6	1.2
C_3	0.6	0.8	3.3
C_4^+	4.7	5.4	11.3

* Avicel 102

APPENDIX 8

ST. LAWRENCE STARCH COMPANY LIMITED
P.O. Box 1050, Port Credit Postal Station,
Mississauga, Ontario L5G 1E8

Telephone: (416) 274-3671
Telex: 06-961142

CUSTOMER SERVICE

APPENDIX 1

ANALYTICAL DATA FOR PEARL 'C' STARCH

Moisture	6 - 8%
pH	4.5 - 5.5
Protein	0.35% max.
Ash	0.1% max.
Specific Gravity (true)	1.5
Particle Size	- less than 5% retained on No. 6 U.S.A. Standard Sieve Series
	- less than 30% passing through No. 60 U.S.A. Standard Sieve Series

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